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# SOIL SCIENCE

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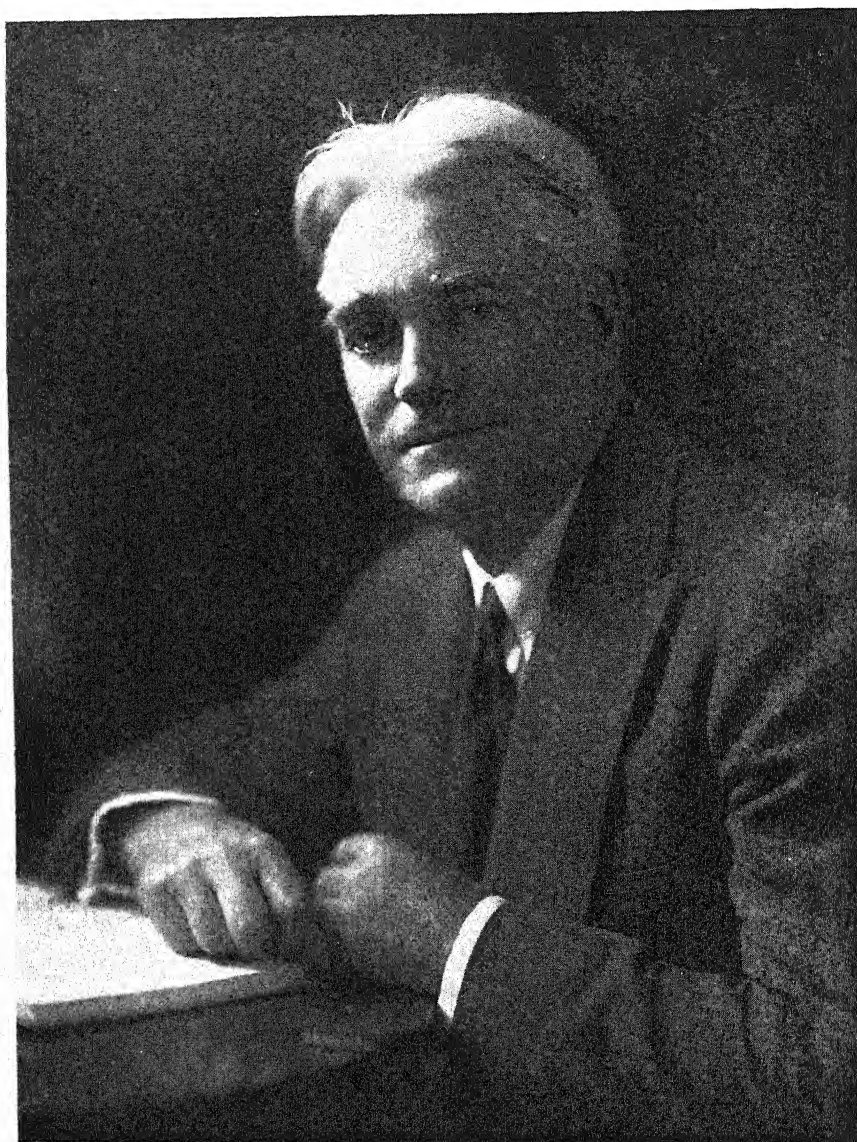
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## CONTENTS

Burton Edward Livingston, 1875-1948. . . . .	1
Great Soil Groups in the Equatorial Regions of Colombia, South America. HANS JENNY. . . . .	5
Structure in Black Cotton Soils of the Nizamsagar Project Area, Hyderabad State, India. P. G. KRISHNA AND S. PERUMAL. . . . .	29
Utilization of Nitrogen in Cropping Systems with and without Green Manure in the Greenhouse. L. A. PINCK, F. E. ALLISON, AND V. L. GADDY. . . . .	39
Testing Soils for Lime Requirement by Means of a Buffered Solution and the Glass Electrode. C. M. WOODRUFF. . . . .	53
Effect of Calcium and Boron Nutrition of the Tomato on the Relation between These Elements in the Tissues. EILEEN G. BRENNAN AND JOHN W. SHIVE. . . . .	65
Books. . . . .	77
Requirements for Successful Soil Tests. ROGER H. BRAY. . . . .	83
Structural Variations of Yangambi (Belgian Congo) Soils. J. D'HOORE AND J. FRIPIAT. . . . .	91
Porous Plate Apparatus for Measuring Moisture Retention and Transmission by Soil. L. A. RICHARDS. . . . .	105
Clay Mineral Models: Construction and Implications. JOHN I. WEAR, JOE E. STECKEL, MAURICE FRIED, AND JOE L. WHITE. . . . .	111
Chemical and Physical Behavior of Copper in Organic Soils. ROBERT E. LUCAS. . . . .	119
Behavior of Manganese in the Soil and the Manganese Cycle. CHARLES K. FUJIMOTO AND G. DONALD SHERMAN. . . . .	131
Magnesium in Fertilizers, Soil Amendments, and Manures. A. L. MEHRING. . . . .	147
Books. . . . .	161
Dimitrii Nikolaevich Pryanishnikov, 1865-1948. . . . .	165
Guy Wollard Conrey, 1887-1948. . . . .	171
Nitrogen and Organic Matter Contents of Equatorial Soils of Colombia, South America. H. JENNY, F. BINGHAM, AND B. PADILLA-SARAVIA. . . . .	173
Molybdenum Content of Pasture Plants in Relation to Toxicity to Cattle. ISSAC BARSHAD. . . . .	187
Toxic Aspect of Molybdenum in Vegetation. W. O. ROBINSON AND GLEN EDGINGTON. . . . .	197
Rapid Conductometric Method for Estimating Gypsum in Soils. C. A. BOWER AND R. B. HUSS. . . . .	199
Determination of the Critical Stream for Various Slopes. WALTER H. GARDNER. . . . .	205
A Fabric Absorption Unit for Continuous Measurement of Soil Moisture in the Field. G. J. BOUYOUCOS AND A. H. MICK. . . . .	217
Effect of Volatile Disinfectants on Survival of Microflora in Soil. FRANK H. DALTON AND CHARLES HURWITZ. . . . .	233
Books. . . . .	239
Modification of Graham's Method for Determining Soil Organic Matter by Colorimetric Analysis. R. CAROLAN. . . . .	241
Analytical Evaluation of Certain Synthetic Organic Phosphates in Relation to Their Fertilizer Effectiveness in Pot Cultures. W. H. MACINTIRE, S. H. WINTERBERG, L. J. HARDIN, A. J. STERGES, AND L. B. CLEMENTS. . . . .	249
Some Effects of Fluorine on Peach, Tomato, and Buckwheat when Absorbed Through the Roots. I. A. LEONE, E. G. BRENNAN, R. H. DAINES, AND W. R. ROBBINS. . . . .	259
Effect of Temperature of Incubation of Amended Soil on Exchangeable Manganese. CHARLES HURWITZ. . . . .	267
Effect of Fumigation, Fertilization, and Various other Soil Treatments on Growth of Orange Seedlings in Old Citrus Soils. JAMES P. MARTIN. . . . .	273
Effect of Cation-Exchange Properties of Soil on the Cation Content of Plants. A. MEHLICH AND J. FIELDING REED. . . . .	289

Effects of Wheat Straw, Lespedeza Sericea Hay, and Farmyard Manure, As Soil Mulches, on the Conservation of Moisture and the Production of Nitrates. C. A. MOOERS, J. B. WASHKO, AND J. B. YOUNG.....	307
The Presence and Determination of Molybdenum and Rare Earths in Phosphate Rock. W. O. ROBINSON.....	317
Potassium-Supplying Power of Virgin and Cropped Soils. C. E. EVANS AND O. J. ATTOE.....	323
✓ Boron Content and Requirements of West Virginia Soils. FRANK W. SCHALLER.....	335
Stony Soils and Their Classification. C. C. NIKIFOROFF.....	347
Soils Developed From Basalt in Western Colorado. JOHN L. RETZER.....	365
Exchangeability of Adsorbed Cations as Influenced by the Degree of Saturation and the Nature of the Complementary Ions with Special Reference to Trace Concentrations. LAMBERT WIKLANDER AND J. E. GIESEKING.....	377
Determination of Magnesium by Thiazol Yellow Method. DUANE S. MIKKELSEN, STEPHEN J. TOTH, AND ARTHUR L. PRINCE.....	385
Persistence of Isopropyl N-Phenyl Carbamate in Soils. ARTHUR S. NEWMAN, H. ROBERT DEROSE, AND HERBERT T. DERIGO.....	393
Effect of Straw Mulch on Recovery of Nitrogen From Nitrate of Soda and Ammonium Sulfate Applied as Top-Dressing. C. A. MOOERS, J. B. WASHKO, AND J. B. YOUNG.....	399
Microbiological Decomposition of Water Hyacinth. A. KARIM.....	401
Influence of Heating on the pH of Soil Suspensions. ROBERT J. CAROLAN.....	417
Influence of Earthworms on Soil Productivity. HENRY HOPP AND CLARENCE S. SLATER.....	421
✓ Determination of Cation- and Anion-Exchange Properties of Soils. A. MEHLICH....	429
✓ A Comparison of Ammonium Acetate and Buffered Barium Chloride Methods for Determining Cation-Exchange Properties of Limed Soils. W. J. HANNA AND J. FIELDING REED.....	447
Rapid Quantitative Determination of Eight Mineral Elements in Plant Tissue by a Systematic Procedure Involving Use of a Flame Photometer. S. J. TOTH, A. L. PRINCE, A. WALLACE, AND D. S. MIKKELSEN.....	459
Books.....	467
Index.....	471





**Burton Edward Livingston**

*Photograph by Eachrach*

## Burton Edward Livingston

1875-1948

On the day before his 73rd birthday, one of the great figures in American biological science, Dr. Burton E. Livingston, Professor Emeritus of Plant Physiology at the Johns Hopkins University, died in Baltimore, Maryland, after a long illness.

Born in Grand Rapids, Michigan, on February 9, 1875, Burton E. Livingston received his early training in the local schools of that state. He then entered the University of Michigan, where he was assistant in botany from 1895 to 1898, receiving the bachelor of science degree in 1898. His postgraduate studies were conducted at the University of Chicago, where he was awarded the Ph.D. degree in 1901.

After completion of his graduate training, Dr. Livingston continued at the university, first as Assistant and then as Associate Plant Physiologist, until 1905, when he accepted the position of Soils Expert in the U. S. Department of Agriculture Bureau of Soils. Dr. Livingston was a member of the staff of the department of botanical research of the Desert Laboratory of the Carnegie Institution of Washington from 1906 to the time of his call to the professorship of plant physiology of the Johns Hopkins University in 1909. Following his official connection with the Carnegie Institution of Washington, it was, for many years, his custom to continue his researches during the summer months at the Desert Botanical Laboratory, Tucson, Arizona, where desert climatic conditions afforded unusual opportunities for the study of water relations of plants, a subject on which Dr. Livingston was the world's leading authority. He held the post of Professor of Plant Physiology of the Johns Hopkins University for 31 years, and from 1913 to the time of his retirement in 1940 he was also Director of the Laboratory of Plant Physiology. From 1931 to 1940 he occupied the chair of the William D. Gill Professorship.

That Dr. Livingston's career was marked by a life-long record of productive scholarship is indicated by the unusual number of original and authoritative research papers which he published. He was the author of nearly two hundred papers on plant physiological subjects, and of several books, including "The Role of Diffusion and Osmotic Pressure in Plants," "The Relation of Desert Plants to Soil Moisture and to Evaporation," and "The Distribution of Vegetation in the United States as Related to Climatic Conditions" (with F. Shreve).

Dr. Livingston was particularly interested in physical processes as related to plant growth. He was a pioneer investigator of the water relations of plants, and he invented many instruments for measuring the physical factors involved in plant growth and development. Among these are the porous cup atmometer for measuring evaporation as a climatic factor, the radio-atmometer for determining the evaporating intensity induced by direct sunlight, the auto-irrigator for the automatic control of soil moisture of potted plants, soil-points for measuring the power of soils to supply water to the roots of plants, and rotating tables for



equalizing environmental conditions about plant cultures. A number of these instruments are now considered throughout the world as standard equipment in plant physiological investigations.

In addition to his primary interest in the physical aspects of plant life, he was also keenly interested in the field of inorganic plant nutrition and the mineral requirements of plants. Dr. Livingston was a recognized leader in this field of investigation. During his long career as an experimental investigator he had a remarkable influence on the progressive development of plant physiology in general in this country and achieved recognition abroad. His researches are remarkable for the thoroughness and care with which they were conducted and for the keen insight and sound judgments displayed in bringing them to completion. Dr. Livingston possessed a remarkable capacity, not only for detecting the problems, but also for recognizing and comprehending their significance. He was always original in his approach to any problem and, by nature, analytical in his observations. His scientific writings are masterpieces of logical thinking. His complete mastery of English, together with great clarity of thought and expression, and thorough, complete, and logical analyses of all matters dealt with, even those of the most complex and abstruse nature, make his writings thoroughly comprehensible and easily understandable to the average reader.

Dr. Livingston was an inspiring teacher of the advanced student. In addition to complete mastery of both subject and language, he possessed the genius to present the material under discussion with such skill and proficiency as to arouse the interest and enthusiasm of the student. The effectiveness of his work as an instructor is evidenced by the large number of young men and women who studied under his guidance and who now occupy positions of prominence and influence in American universities and colleges. A man of many and unusual talents, Dr. Livingston will long be remembered as a counselor of students about to enter upon a career of scientific endeavor, as an ambassador of good will for the many professional organizations in which he held positions of influence and prominence, and as one of the leading builders of the science to which he was devoted.

Dr. Livingston held many positions of importance, and to all of them he brought ability, understanding, and inspiration. Many well-deserved honors were bestowed upon him by the membership of the professional organizations to which he belonged. He was permanent secretary of the American Association for the Advancement of Science from 1920 to 1931, general secretary from 1931 to 1934, and member of the executive committee from 1920 to 1944, chairman in 1941. The phenomenal growth and development of the American Association during and following the years of Dr. Livingston's incumbency as secretary must be attributed largely to the remarkable executive ability and sound judgment which he brought to the work of framing the broader policies of the Association, as well as the skill and tireless energy displayed in managing the innumerable details of administration. The many excellent policies brought into effective operation through Dr. Livingston's leadership while he was secretary of the American Association left their imprint not only upon the association but also

upon the more than one hundred affiliated organizations, and imparted an influence for progressive development upon science and education in America which will not soon be forgotten. He was a member of the Botanical Society of America, the Ecological Society of America, the American Society of Naturalists, serving as its president in 1934. He was a member of the National Research Council from 1917 to 1918, Committee on Foreign Relations from 1920 to 1930. He was a fellow of the American Academy of Arts and Sciences and a member of the American Philosophical Society. He was the recipient of the Walker Prize of the Boston Society of Natural History in 1903. He was Collaborator in the U. S. Forest Service in 1902, managing editor of *Physiological Researches* from 1913 to 1923, editor-in-chief of *Botanical Abstracts* from 1918 to 1920, and consulting editor of *SOIL SCIENCE* from 1918 to the time of his death.

Dr. Livingston was a charter member of the American Society of Plant Physiologists, and to this organization he gave the same unselfish devotion and service which characterized his activities in the American Association for the Advancement of Science. It was largely through his keen judgment and unusual foresight that the sound fiscal, administrative, and scientific literary policies, and the durable character of the society's constitution, as drafted by him, were so promptly established during the very early years of the Society's existence. In recognition of his "eminence as a scholar" and as "an appreciative tribute to his unselfish service to science," he was awarded the first Charles Reed Barnes Life Membership in the Society in 1926, and was elected president of the Society in 1934, to membership in the executive committee, and to the editorial board of the journal *Plant Physiology*. As further recognition of his deep loyalty and distinguished services, the Society awarded him the Stephen Hales prize in 1946.

Those who had the good fortune to be associated with Dr. Livingston in any capacity were deeply impressed by his charming personality, by his sterling qualities, and by the depth of his knowledge and the breadth of his outlook upon human affairs in general. It was this understanding of problems and individuals, coupled with a keen sense of humor and an innate generosity, which accounted for his great charm as a conversationalist. His skill in the training of students for leadership in science and education and his great talents for research and administration brought international fame to himself, to the great institution which he served so well for so many years, and to the science to which he gave a lifetime of devotion.

JOHN W. SHIVE





# GREAT SOIL GROUPS IN THE EQUATORIAL REGIONS OF COLOMBIA, SOUTH AMERICA

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Received for publication March 19, 1948

Several groups of investigators are studying the soils of Colombia, S. A., from agronomic and pedologic viewpoints. Probably the earliest systematic field and laboratory studies were instigated by the Centro Nacional de Investigaciones de Café under the leadership of P. Schaufelberger. For a number of years, J. Ancizar-Sordo, director of the Laboratorio Químico Nacional, has been instrumental in fostering physical and chemical soil analyses. The Instituto Geográfico, Militar, y Catastral is conducting detailed soil surveys under the direction of J. V. Lafaurie-Acosta. A. Franco-Urbe of the Caja de Crédito Agrario Industrial y Minero is studying soils mainly from the irrigation standpoint, whereas Dean Carlos Madrid S. of the Facultad de Agronomía in Medellín stresses modern methods of teaching soil science.

For nearly half a year the author had the unique opportunity and the pleasure of working with these groups in the field and laboratory. In view of the possibility that a knowledge of equatorial soils will advance the understanding of soils of northern latitudes, especially the United States, an attempt is herewith made to give a brief outline of the broader aspects of soil groupings in Colombia.

## CLIMATIC VALUES OF COLOMBIA

Monthly values of rainfall, temperature, and relative humidity have been published by the Ministerio de la Economía Nacional in the *Anuario Meteorológico*. For the present study, values for the 12-year period 1933-1944 were used. In addition, some unpublished data also were available.

The following annual climatic characteristics were calculated for 35 stations (table 1): precipitation ( $P$ ), temperature ( $T$ ), relative humidity ( $H$ ), Lang's rain factor ( $RF$ ), Meyer's N.S.Q., and Thornthwaite's precipitation effectiveness ( $PE$ -index) and temperature efficiency index ( $TE$ -index).<sup>2</sup> The relationships between the various moisture factors and the precipitation ( $P$ ) expressed in millimeters were calculated according to the method of least squares. They are of the following form:

$$\begin{aligned} RF &= 0.04 P + 5, (r = 0.95) \\ NSQ &= 0.233P - 54, (r = 0.88) \\ PE &= 0.06P - 10, (r = 0.90) \end{aligned}$$

In calculating the last equation, the per-humid station Quibdó was omitted.

<sup>1</sup> The author is indebted to the John Simon Guggenheim Memorial Foundation and the Ministerio de Minas y Petróleos, Bogotá, for financial support, and to the Federación Nacional de Cafeteros de Colombia for providing living quarters in Chinchiná and assistance on expeditions.

A close relationship exists between mean annual temperature and elevation. On the basis of data from more than 100 Colombian stations, the following free-

TABLE 1  
*Climatic values of selected Colombian stations*

STATION AND ITS ABBREVIATION	ELEVA- TION	MEAN ANNUAL PRECIPI- TATION	MEAN ANNUAL TEMPER- ATURE	MEAN ANNUAL RELA- TIVE HUMID- ITY	N.S.Q.	PE	TE	RAIN FACTOR
	<i>m.</i>	<i>mm.</i>	<i>°C.</i>	<i>per cent</i>				
Acacias (Meta), Ac.....	517	5053	23.9	79	1082	301	129	211
Armero (Tolima), Ar.....	421	1818	27.4	73	246	88	148	66
Barrancabermeja (Sant.), Ba.....	82	2938	29.3	78*	437*	145	158	100
Barranquilla (Atlántico), Barr.....	4	893	28.1	80	156	41	152	32
Bogotá (Cundinamarca), Bo.....	2640	976	14.5	69	254	68	78	67
Cali (Valle del Cauca).....	957	1213	24.3	64	148	62	131	50
Cartagena (Bolívar), Ca.....	4	1081	27.8	80	193	51	150	39
Cartago (Valle del Cauca), Cart....	880	1586	24.2	68	228	83	131	66
Chinchiná (Caldas), Ch.....	1433	2769	22.0	75	558	164	119	126
Córdoba (Valle del Cauca), Co.....	37	4678	26.1	80*	922*	262	141	179
Espinal (Tolima), Esp.....	438	1500	27.7	72	192	70	150	54
Florencia (Caqueta), Fl.....	300*	3469	26.4	84	837	191	143	131
Fómeque (Cundinamarca), Fo.....	1933	566	17.1	76	161	35	92	33
Girardot (Cundinamarca), Gir.....	330	1319	30.0	64	115	57	162	44
Ibagué (Tolima), Ib.....	1250*	2081	22.3	77	448	120	120	93
La Petrolea (Norte de S.), LP.....	90*	3117	28.0	75	439	158	151	111
Magangué (Bolívar), Ma.....	27	3841	30.7	75	463	191	166	125
Manizales (Caldas), Man.....	2153	2045	17.1	75	560	144	92	119
Mariquita (Tolima), Mar.....	535	2366	26.2	75*	370*	124	142	90
Medellín (Antioquia), Med.....	1538	1443	21.9	67	222	81	118	66
Natagaima (Tolima), Na.....	316	1267	29.2	70	139	58	158	43
Neiva (Huila), Nei.....	431	1239	27.2	72	163	57	147	46
Palmira (Valle del Cauca), Pal.....	1066	956	24.0	70	142	48	130	40
Pasto (Nariño), Pas.....	2594	868	16.0	72	227	59	86	54
Popayán (Cauca), Po.....	1760	1627	19.2	70	325	102	104	85
Quibdó (Chocó), Qui.....	54	13078	27.3	84	2997	480	147	479
Regadera de Bogotá (Re.).....	3200	972	9.1	83	671	89	49	107
Riohacha (Magdalena), Río.....	10*	789	31.5	65*	65*	34	170	25
St. Rosa de Cabal (Caldas), SRC...	1800	1859	20.0	79	504	115	108	93
Sibundoy (Putumayo), Si.....	2224	4553	15.2	81	1851	361	82	302
Sucre (Caquetá), Su.....	1025	2518	21.3	88	671	153	115	118
Tunja (Boyacá), Tu.....	2820	811	13.0	75	289	60	70	62
Uribia (La Guajira), Ur.....	40*	433	26.9	62	43	19	145	16
Villavicencio (Meta), Vv.....	498	4033	26.3	76	654	223	142	153
Yarumal (Antioquia), Yar.....	2300	2144	16.8	75	597	151	91	128

\* Indicates approximations.

It is impossible to acknowledge satisfactorily all the help and information which the author received from individuals. The field work was greatly aided by the cooperation of P. Schaufelberger, L. O. Souffront, J. Hernández, F. Irusta, A. Franco, and V. M. Patiño.

<sup>2</sup> Many of the tedious compilations and calculations were made by E. H. Hammond.

hand curve was drawn:<sup>3</sup>

$$T = -0.0057 E + 29$$

The letter  $T$  denotes mean annual temperature in centigrades, and  $E$  the elevation in meters. According to this equation, the average mean annual temperature at sea level would be 29°C. (84°F.). Along the humid west coast it is lower, whereas in the dry, hot valleys it may rise to 30°C. (86°F.). The 0°C. isotherm (32°F.) which corresponds approximately to the perpetual snow line would occur at 4,900 m. (16,076 feet). According to Dugand (3, pp. 289-293) the timberline occurs at an elevation of 3,200-3,800 m. (10,500-12,500 feet). This would correspond to an annual temperature of 7-11°C. (45-52°F.). The approximate lower limit of perpetual snow occurs between 4,500 and 4,800 m.

For all soils examined, the elevation was measured with a barometer, and the annual temperature was then calculated from the nearest meteorological station, the interval 0.57°C. per 100 m. being used as a basis. Rainfall values had to be interpolated from surrounding stations, a procedure which may have introduced considerable error.

#### CLIMATIC FIELDS

To compare graphically certain climatic aspects of Colombia with those of the United States, "climatic fields" were constructed which portray the range of two annual climatic variables such as rainfall and temperature, or precipitation effectiveness and temperature-efficiency.

For the temperature-precipitation field ( $TP$ -field) the mean annual temperature of a station is plotted as ordinate, and its mean annual precipitation as abscissa. Each meteorological station appears thus as a point in the  $TP$  system of coordinates. The scattering of the various points constitutes a climatic field which is characteristic of the area in question.

Figure 1 shows the  $TP$ -fields of Colombia and of the United States east of the Rocky Mountains. Though the climatic fields of both countries overlap considerably, Colombia by far exceeds the United States in the moisture range. This discrepancy suggests that Colombia may possess a series of climatic soil types or zonal soils which do not occur in the United States.

#### CLIMATIC DISTRIBUTION OF VEGETATION

With the exception of the dry region of the Guajira Peninsula and adjoining parts of the Caribbean Coast, most of the tropic, subtropic, and temperate regions are, or were, covered with luxuriant forests. Certain isolated areas such as the Savanna of Bogotá and portions of the Llanos of eastern Colombia were treeless when the Spanish conquerors arrived, but there are good reasons for believing that these grasslands were not conditioned by climate. Xerophytic vegetation also exists in the upper Magdalena Valley near Neiva. The climate,

<sup>3</sup> According to the method of least squares the temperature-elevation equation for the stations listed in table 1 is as follows:

$$T = -0.00564 E + 29.12 \quad (r = 0.97)$$

The standard error of estimate has a value of 1.40.

however, lacks extreme aridity. Cuatrecasas,<sup>4</sup> a botanist, is inclined to believe that, in Colombia, regions with more than 700 mm. (27.6 inches) of rainfall were originally forested.

#### COLLECTING AND ANALYZING SOIL SAMPLES

The regions investigated are shown in Figure 2.

Surface and subsoil samples were taken with a spade, whereas examination and collection of deeper strata had to be restricted to recent cuts and exposures. A

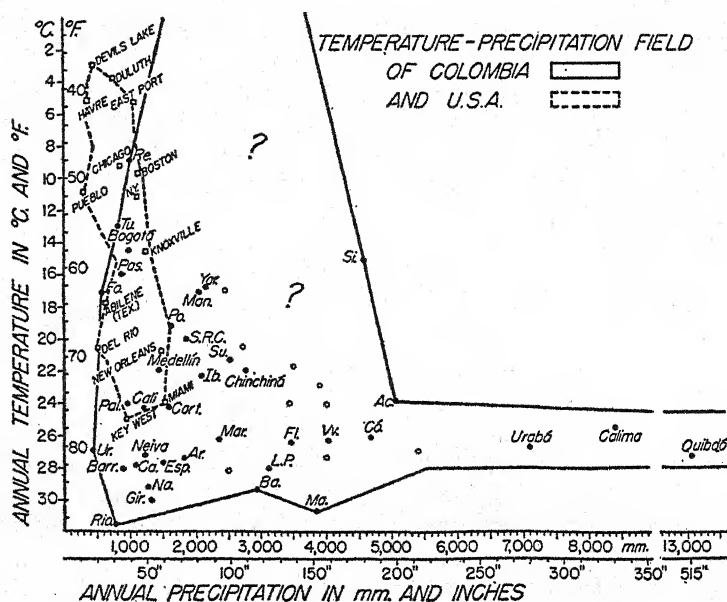


FIG. 1. ANNUAL TEMPERATURE AND ANNUAL PRECIPITATION DIAGRAMS OF COLOMBIA AND OF THE UNITED STATES EAST OF THE ROCKY MOUNTAINS

On the vertical axis decreasing temperature corresponds to increasing elevation in Colombia and increasing latitude in the United States.

square steel frame was used to obtain samples of forest floor on an areal basis. The soils were placed in cloth bags and carried or shipped in moist conditions to the pedological laboratory of the Coffee Experiment Station in Chinchiná (Caldas). The samples were then air-dried, and the coarse rock particles were separated with the aid of a 2-mm. sieve. Care was taken to remove as many roots and rootlets as possible. The samples were then sent to Berkeley, California.

Total nitrogen was determined according to the Kjeldahl method, total organic carbon by the dry combustion method, and pH with the glass electrode.<sup>5</sup> Two types of pH readings were taken: one in a soil suspension having a soil-water

<sup>4</sup> Personal communication.

<sup>5</sup> Determinations by F. T. Bingham.



ratio of 1:2, the other in a soil paste. The results by the two methods seldom differed by more than 0.1 or 0.2 pH unit. In all tables the pH value refers to the 1:2 soil-water ratio. Nitrogen and carbon are expressed on an oven-dry basis.

Texture was determined in the laboratory by the feel method. For color analysis the dry soil samples were placed on a white piece of paper and pressed with a spatula to create a smooth surface. In broad daylight the soil colors were then matched with the new color chart distributed by the Division of Soil Survey of the Bureau of Plant Industry, Soils, and Agricultural Engineering. The color specifications listed in the tables correspond to the Munsell notation.<sup>6</sup>

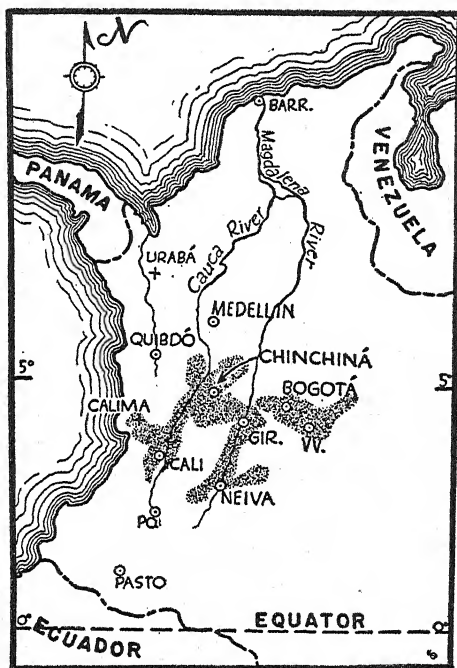


FIG. 2. SKETCH OF COLOMBIA, SHOWING REGIONS INVESTIGATED (DOTTED AREAS)

#### PRESENT STATUS OF SOIL CLASSIFICATION IN COLOMBIA

In a generalized discussion of South American soils, Hardy (5, pp. 322-326) distinguishes in Colombia the following zonal and azonal soils: red earth, bleached earth, lithosols, and alluvial soils.

Lafaurie (8) and his group have mapped in Cundinamarca the following soil groups: wiesenboden, planosol, rendzina, brown podzolic soils, gray-brown podzolic soils, lithosols, alluvial soils, and yellow-brown podzolic soils. In other parts of Colombia, Lafaurie surmises the existence of desert soils, red chestnut soils, chernozems, prairie soils, laterites, brown-red laterites, and brown-yellow laterites. Although Lafaurie made an earnest attempt to fit the Colombian soils into

<sup>6</sup> Many of the color determinations were made by E. H. Hammond.

the North American scheme of great soil groups, he had to introduce at least one new group, the yellow-brown podzolic soils.

Schaufelberger (12) has constructed a soil map which is more detailed than Hardy's. He delineates soils of the arid climate, brown soils, black soils, soils of the cold climate, swampy soils, laterities, ortstein, and alkaline soils. Though Schaufelberger's classification is unorthodox and unfamiliar to North Americans, it has the advantage of being free of bondage from systems evolved outside the tropics.

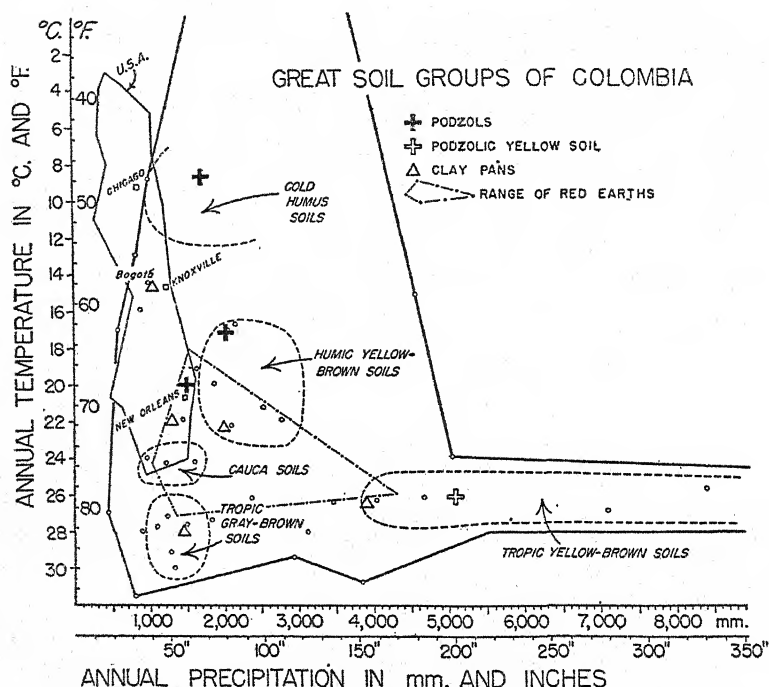


FIG. 3. GREAT SOIL GROUPS IN COLOMBIA IN RELATION TO CLIMATE

On the vertical axis, decreasing temperature corresponds to increasing elevation in Colombia.

#### BRIEF DESCRIPTION OF SOME GREAT SOIL GROUPS IN COLOMBIA

*Great soil groups* may be defined as assemblages or groups of soil series having similar profile features. The soil series belonging to great soil groups usually possess characteristic constellations of soil-forming factors.

In the temperature-precipitation field of figure 3 are sketched a number of great soil groups. In considering their areal extent it should be remembered that the climatic field of a soil group does not correspond to its surface area. A land area comprising 1,000 square miles of uniform climate would be represented in figure 3 by a point only. On the other hand, a large climatic field may be contained in a small physical area, as exemplified by the climatic range along a steep mountain slope.

The following groups of soils are briefly discussed: cold humus soils, podzols, humic yellow-brown soils, Cauca Valley soils, tropic gray-brown soils, tropic yellow-brown soils, podzolic yellow soils, red earths, claypan soils, hardpan soils, and rendzinas.

*Cold humus soils (psychrohumus soils)*

Near and above the timberline, where the climate is uniformly cold and foggy throughout the year, soils resembling alpine humus soils are encountered. The acid, dark colored organic matter horizon is the outstanding profile feature. The soils are usually shallow. They possess good water permeability. The humus accumulation appears to be the result of prevailing low temperatures rather than excessive moisture conditions.

TABLE 2  
*Andino humus soil*  
(Depresión profile, No. 41)

*Locality:* Depresión, between Armenia and Ibagué, elevation 3,200 m. (10,500 feet).

*Climate:* estimated, temperature 11°C. (52°F.), precipitation 2,000 mm. (79 inches).

*Vegetation:* Vaccinium, and sphagnum moss.

*Topography:* level spot on steep mountain slope, well drained.

*Parent material:* gravelly volcanic tuff (postglacial).

*Profile description:*

DEPTH	HORIZON AND TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
0-6	Humus layer, loamy	Dark brown, 7.5 YR 3/2	2.66	41.62	15.7	3.3
6-10	Humus layer, sandy loam	Dark gray, 10 YR 4/1	1.79	24.58	13.7	3.4
10-15	Humus layer, sandy loam	Grayish brown, 10 YR 4/2	0.44	8.02	18.2	4.7
15-18+	Sandy loam, with $\frac{1}{4}$ -inch Fe-bands	Yellowish loam, 10 YR 5/4	0.15	3.63	24.2	5.3

The *andino humus soil* (table 2) observed at Depresión approaches the alpine humus soil most closely. The presence of iron oxide bands in the C horizon suggests the presence of a concealed podzol. Shallow humus soils may also be seen on the steep path from Bogotá to Monserrate. At 3,200 m. elevation on a slope of over 100 per cent a sample had a pH of 4.0; the total nitrogen content was 0.70 per cent; the organic carbon content 10.64 per cent. The climate corresponds to that of the Regadera de Bogotá (see table 1) with an annual temperature of 48°F. and an annual rainfall of 38 inches. The name "andino humus soils" (from Andes) has been chosen to indicate possible systematic deviations from alpine humus soils.

*Páramo humus soils* do not occur in the Alps, but they are common in Colombia. In comparison to the andino humus soils the profile is deeper and the humus layers are less sharply segregated.

Table 3 gives analytical data on three páramo humus soils, collected in the



## Páramo de Bavaya, central Cordillera:

Q-10: Elevation 3,540 m. (11,600 feet). Vegetation: *Espeletia Hartwegiana*, and *Calamagrostis*. Parent material consists of mica schist and amphibolite schist.

Q-11: Elevation 3,450 m. (11,300 feet). Vegetation: nearly virgin páramo forest with *Hesperomeles ferruginea* and *Weinmannia*, *Hydrocotyle* (*Poa annua*). Parent material consists of quartz and mica schist.

Q-12: Elevation 3000 m. (9,800 feet). Dense cover of *graminaes*, *Dactylis glomerata*.

TABLE 3

## Páramo humus soils

Collected by J. Cuatrecasas

PROFILE NUMBER	DEPTH OF SAMPLING	TEXTURE	COLOR	N	C	C/N	pH
	inches			per cent	per cent		
Q-10	0-6	Sandy loam	Black, 2.5 YR 2/0	1.82	29.87	16.4	4.3
	6-18	Fine sandy loam	Black, 10 YR 2/1	0.92	15.67	17.0	4.4
	18-26	Gravelly loam	Dark gray, 2.5 Y 4/1	0.29	4.69	16.2	4.3
	26-47	Gravelly loam	Olive-gray, 5 Y 5/2	0.19	1.70	9.0	4.5
Q-11	0-4	Loam	Dark reddish brown, 5 YR 2/2	1.55	25.06	16.2	3.7
	4-24	Gravelly fine sandy loam	Dark grayish brown, 10 YR 3/2	0.75	12.61	16.8	3.9
	24-32	Gravelly fine sandy loam	Grayish brown, 2.5 Y 5/2	0.29	3.26	11.2	4.3
	32-62	Gravelly fine sandy loam	Olive-yellow, 2.5 Y 6/5	0.18	1.47	8.2	4.4
Q-12	0-4	Fine sandy loam	Black, 10 YR 2/1	1.48	18.48	12.5	5.6
	10-18	Fine sandy loam	Black, 10 YR 2/1	0.69	12.76	18.5	4.8
	at 28	Fine sandy loam	Dark grayish brown, 10 YR 3/2	0.44	8.05	18.3	4.9
	39-47	Loamy fine sand	Grayish brown, 10 YR 4/2	0.24	4.93	20.5	5.2
	at 67	Loamy fine sand	Yellowish brown, 10 YR 5/5	0.21	3.13	14.9	5.4

The soils are very acid. Their nitrogen and organic matter contents are very high, and the carbon-nitrogen ratio is wide. During excavation, water began to seep into the bottoms of the holes.

## Podzols

Near the timberline, at an elevation of nearly 12,000 feet, podzols are encountered. These *andino podzols* (table 4) have a strongly developed raw humus horizon ( $A_0 + A_1$ ). Their dwarflike nature is similar to that of the alpine podzols in central Europe.

In the vicinity of the town of Albán near Bogotá, Lafaurie and associates have described and mapped the Sabaneta series, which they classify tentatively as a gray-brown podzolic soil (8). The writer would go a step further and pronounce

TABLE 4

*Andino podzol*

Letras profile, No. 37

*Locality:* Letras, east of Manizales (Caldas), elevation 3600 m. (11,740 feet).*Climate:* estimated, temperature 9°C. (48°F.), precipitation 1,700 mm. (67 inches).*Vegetation:* Alpine herbs and grasses, *Vaccinium*.*Topography:* undulating broad ridge, slope 1-3 per cent, well drained.*Parent material:* gravelly volcanic tuff (postglacial).*Profile description:*

DEPTH	HORIZON DESIGNATION	TEXTURE, ETC.	COLOR	N	C	C/N	pH
<i>inches</i>				<i>per cent</i>	<i>per cent</i>		
0-6	A <sub>0</sub> +A <sub>1</sub>	Organic sandy loam	Dark gray-brown, 10 YR 3/2	1.11	25.42	22.9	4.7
6-8	A <sub>2</sub>	Fine sandy loam	Grayish brown, 10 YR 4/2	0.33	5.47	16.6	5.1
8-9	B	Coarse grit	Brown, 10 YR 5/3	0.08	1.30	16.3	5.4
9-15+	C	Coarse grit	Pale yellow, 2.5 Y 7/4	0.03	0.50	16.7	5.4

TABLE 5

*Giant podzol*

Sabaneta series, No. 94

*Locality:* near Albán (Cundinamarca), elevation 2460 m. (8,070 feet).*Climate:* estimated, temperature 17°C. (63°F.), precipitation 2,000 mm. (79 inches).*Vegetation:* now pasture, originally forest with a dense cover of ferns.*Topography:* gently sloping fan, slope 5-10 per cent.*Parent material:* rock debris consisting of sandstones and shales of Tertiary age.*Profile description:*

DEPTH	HORIZON	TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>				<i>per cent</i>	<i>per cent</i>		
0-18	A <sub>1</sub>	Very fine sandy loam	Grayish brown, 10 YR 4/2	0.88	9.75	11.1	5.3
18-32	A <sub>2</sub>	Sandy loam	Pale brown, 10 YR 6/3	0.32	4.97	15.5	5.4
32-45		Sandy loam	Light gray, 2.5 Y 7/2	0.19	3.58	18.8	5.6
45-56		Fine sandy loam	White, 2.5 Y 8/3	0.15	2.40	16.0	5.7
Half-inch		chocolate colored band					
56-60	B <sub>1</sub> iron-horizon	Fine sandy loam	Yellowish red, 5 YR 5/8	0.10	4.21	42.1	5.6
68-80	B <sub>2</sub>	Very fine sandy clay loam	Yellow, 10 YR 8/6	0.09	1.45	16.1	5.3
80+	C	Sandstone	White inside, reddish yellow coated	....	....	....	...

these profiles podzols; in fact, in some localities they assume the dimensions of *giant podzols* (table 5). The gigantic proportions are symbolized by the gray A<sub>2</sub> horizon which has a thickness of over 3 feet. The B<sub>1</sub> horizon also is spec-

tacular. It is represented by a solid band of laminated iron oxide, 3 to 5 inches thick. The iron band seems to follow the configuration of the present soil surface, thus excluding the possibility of its being a geological deposit or stratum. At present L. Rojas-Cruz is analyzing this profile in greater detail in the writer's laboratory. A very similar profile, but apparently of only local extent, was dis-

TABLE 6

*Humic yellow-brown soil*  
Chinchiná profile, No. 73

*Locality:* Granja Chinchiná (Caldas), elevation 1630 m. (5350 feet).

*Climate:* approximate, temperature 21°C. (70°F.), precipitation 2,800 mm. (110 inches).

*Vegetation:* luxuriant forest (broad-leaf).

*Topography:* broad mountain ridge, slope 0-3 per cent, well drained.

*Parent material:* volcanic ash (Pleistocene).

*Profile description:*

DEPTH*	HORIZON DESCRIPTION, TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
-2.5 to 0	Fresh and half decomposed leaves 7.5 tons per acre		1.43	48.19	33.7	6.2
0-8	Sandy loam	Grayish brown, 10 YR 4/2	0.78	10.50	13.5	5.8
8-12	Fine sandy loam	Grayish brown, 10 YR 4/2	0.64	7.09	11.1	5.8
12-16	Fine sandy loam	Brown, 10 YR 5/3	0.34	4.35	12.8	6.0
16-20	Sandy loam	Light yellowish brown, 10 YR 6/4	0.18	2.23	12.4	6.1
20-26+	Sandy loam	Pale yellow, 2.5 Y 7/4	0.14	1.80	12.9	6.1

\* Layers above the mineral soil are designated with negative numbers.

covered in the region of red earths on diabase rock near kilometer 18 from Cali on the road to Buenaventura:

- 0-8 inches A<sub>1</sub> grayish brown loam.
- 8-12 inches A<sub>1</sub> fading out of organic matter.
- 12-20 inches ? yellow sandy loam.
- 20-36 inches ? reddish yellow (7.5 YR 6/9) sandy loam (0.17 per cent N, pH = 5.2).
- 36-74 inches A<sub>2</sub> pale yellow (2.5 Y 8/4) clayey sand (0.07 per cent N, pH = 5.7).
- 74-76 inches B<sub>1</sub> yellowish red hematite band (pH 5.5).
- 76-100+ inches B<sub>2</sub> reddish soil with purple tint, containing many white spots, clay loam.

Parent rock: diabase.

*Humic yellow-brown soils*

In Caldas and adjoining states are found extensive bodies of well-drained soils, having zonal character. These soils are properly designated as humic yellow-brown soils (tables 6 and 7). The outstanding profile features are a deep, grayish brown (when dry) or black (when wet) humus horizon resting on light colored

yellow, brown, or yellowish brown subsoils. No marked clay accumulations are detectable in the field, and podzolization either by color or structure criteria is not visible.

The dark humus horizon varies in thickness from 15 to 30 inches, the range 18 to 25 inches being very common. It fades rather suddenly into the light colored subsoil strata over a depth interval of only 5 to 7 inches. The extent of the humus horizon appears to be largely independent of slope, even if the latter assumes magnitudes of 50 to 100 per cent, which are frequent in the agricultural regions.

The parent material is predominantly andesitic volcanic ash of Pleistocene age,<sup>7</sup> having loess-like character. Typical profiles were also found on colluvial mate-

TABLE 7  
*Humic yellow-brown soil*  
Pereira profile, No. 5

*Locality:* airport Pereira (Caldas), elevation 1470 m. (4820 feet).

*Climate:* approximate, temperature 22°C. (72°F.), precipitation 2400 mm. (94 inches).

*Vegetation:* originally broad-leaf forest, now pasture and brush.

*Topography:* undulating, slope 2-3 per cent, well drained.

*Parent material:* volcanic ash (Pleistocene).

*Profile description:*

DEPTH	TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
0-6	Loam	Grayish brown, 2.5 Y 5/2	0.63	6.72	10.7	5.5
6-12	Fine sandy loam	Grayish brown, 10 YR 4/2	0.58	6.02	10.4	5.3
12-18	Fine sandy loam	Brown, 10 YR 5/3	0.40	4.82	12.1	5.6
18-24	Fine sandy loam	Pale brown, 10 YR 6/3	0.34	3.12	9.2	5.6
24-30	Fine sandy loam	Pale yellow, 2.5 Y 7/4	0.24	2.55	10.6	6.0
30-36	Fine sandy loam	Pale yellow, 2.5 Y 7/4	0.17	2.63	15.5	6.2
36-43	Sandy loam	Pale yellow, 2.5 Y 7/4	0.18	2.26	12.6	6.1
48-60	Sandy loam	Pale yellow, 2.5 Y 7/4	0.14	1.85	13.2	6.1

rial, alluvial fans, quartz schists, shales, soft sandstones, and dioritic alluvial strata. The latter produce a more reddish colored variant (region of Ibagué). American observers are struck by a similarity with prairie soils. There are, however, a number of significant features which justify a separation from the prairie soils.

Obviously, the climatic and biotic soil-forming factors are different. The annual temperature is higher; for the localities examined it ranges from 17 to 23°C. (63 to 73°F.). The precipitation also is higher, ranging from 1,800 to 2,800 mm. (70 to 110 inches). Derived climatic variables are as follows:  $PE = 100 -$

<sup>7</sup> According to F. Irusta (personal communication), on very old ash deposits clay accumulations in the subsoil become noticeable. Simultaneously the nitrogen content declines (Nápoles series). These might be representative of Lafaurie's yellow-brown podzolic soils (8).

170,  $TE = 90-130$ ,  $NSQ = 300-600$ ,  $RF = 80-130$ . Unlike the prairie soils, all humic yellow-brown soils have formed under a dense, luxuriant tropical forest.

Compared with Midwestern and Californian prairie soils the pH values of the humic yellow-brown soils indicate a somewhat higher acidity. Values between 4.8 and 5.6 are common for surface soils. The average pH of 15 samples was 5.5 for the 1:2 soil-water ratio and 5.4 for the paste method.

The nitrogen and organic matter content of the humic yellow brown soils exceeds that of the prairie soils severalfold. To a depth of 8 inches the average

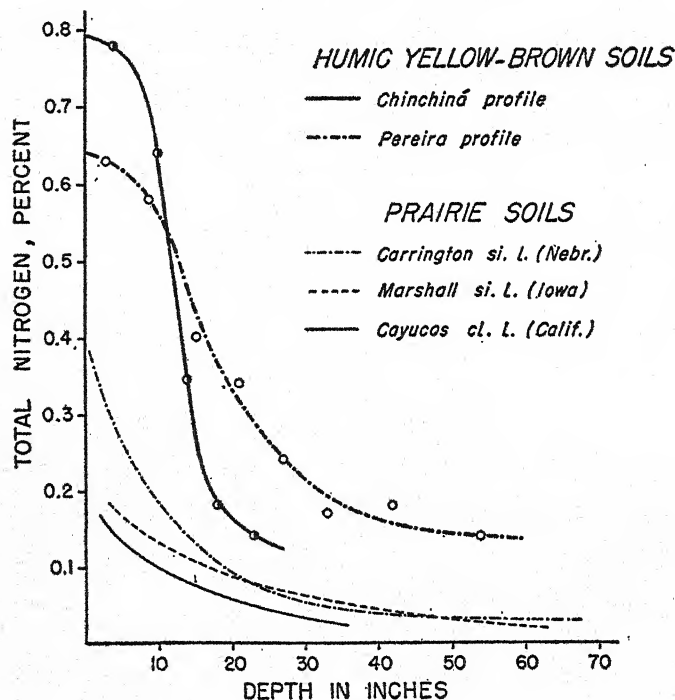


FIG. 4. NITROGEN-DEPTH FUNCTIONS OF HUMIC YELLOW-BROWN SOILS, AND PRAIRIE SOILS

Prairie soils according to Barshad (1), Marbut (10), and Russel (11).

nitrogen and organic carbon content of 15 virgin and cultivated soils amounts to 0.56 per cent N and 6.23 per cent C.

Whereas the nitrogen depth function of prairie soils, especially of those on loessial material, has a simple diffusion-like pattern, that of humic yellow-brown soils on physically similar parent material (volcanic ash) exhibits an S-type curve, as illustrated in figure 4.

According to Franco's description (4) of the soils of the Popayán area these also may belong to the humic yellow-brown soils.

#### *Soils of Cauca Valley*

Cauca Valley lies between west and central Cordillera at an elevation of about 3,000 feet. Soils were examined in the vicinities of Cali, Palmira, and north of



Cartago. For these localities the annual temperature is about 23–24°C. (73–75°F.) and the annual precipitation 1,000–1,500 mm. (39–59 inches). These annual climatic values correspond to those of southern Florida.

The color of the surface soils varies from pale brown, light yellowish brown, to grayish brown. The subsoils are more brilliantly brown or yellow colored. East of Cali, Lafaurie and his group are conducting detailed soil surveys. Their Miranda series, derived from coarse, basic igneous alluvium, looks identical with the Sweeney series, a prairie soil, in California. As judged by chemical analysis, the Candelaria series corresponds to a chernozem. The entire valley was originally forested, however, according to Ciro Molina-Garcés.<sup>8</sup> The analysis of nine surface soils to a depth of 8 inches gave the following results:

		Average	Extremes
Total nitrogen.....	Per cent	0.28	0.22– 0.36
Organic carbon.....	Per cent	3.13	2.42– 5.46
C:N.....		11.2	9.1 –15.2
pH (1:2).....		5.8	5.7 – 6.2
pH (paste).....		5.6	5.4 – 6.0

The term *Cauca soils* has only a geographic meaning. The author's soil examinations were too cursory to permit pedological differentiation and classification of the area. It is probable, however, that the lime-free members of the Cauca group constitute a climosequence with the humic yellow-brown soils, which belong to a somewhat cooler and more humid climate.

#### *Tropic gray-brown soils*

In the upper Magdalena Valley, between Girardot and Neiva, a group of soils has developed which differs markedly from those of other parts of Colombia. The climate is hot and semihumid to semiarid. The annual temperature varies between 27 and 30°C. (81 and 86°F.) and the annual rainfall from 1,200 to 1,500 mm. (47 to 59 inches). The original vegetation probably consisted of forest, but now scrubby trees, cacti, and other xerophytic plants occupy the uncultivated areas.

In contrast to other Colombian soils, the outstanding feature of these "tropic gray-brown soils" is their relatively low content of organic matter, as seen from the following summary of surface soils (0–8 inches):

	NITROGEN		ORGANIC CARBON		C/N
	Average	Range	Average	Range	
	per cent	per cent	per cent	per cent	
Soils under forest or brush (8 samples).....	0.14	0.08–0.19	1.49	0.96–2.07	11.2
Cultivated fields (4 samples).....	0.09	0.02–0.12	1.04	0.21–2.17	

Absence of a distinct organic horizon results in considerable uniformity of color within the profile. The color is gray (table 8), gray-brown, or brown (table

<sup>8</sup> Personal communication.

9), presumably depending on parent material, which consists of river alluvium, shale, or volcanic tuff. No marked development of a B horizon is noticeable. Structural features within the profile are not conspicuous. A good account of these soils has recently been given by Franco (4).

Soil reaction corresponds to an average pH of 6.3, with extremes ranging from pH 5.3 to 7.2. In the Saldaña and Espinal areas Colombian soil surveyors observed soils having lime in the subsoil, but the writer has not encountered calcareous soils. On the high-lying, older terraces between Neiva and Baraya the soils tend to be more reddish brown and also, especially near Melgar, more acid (pH 4.8).

TABLE 8

*Tropic gray-brown soil*

Chicoral profile, No. 46; Coello soil series, No. 14

*Locality:* between Chicoral and Espinal (Tolima), elevation 450 m. (1,476 feet).

*Climate:* Espinal, temperature 27.7°C. (82°F.), precipitation 1,500 mm. (59 inches).

*Vegetation:* originally forest, now pasture.

*Topography:* slightly undulating, slope 1 per cent.

*Parent material:* old terrace consisting of volcanic tuff.

*Profile description:*

DEPTH	REMARKS	PARTI- CLES > 2 MM.	TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>		<i>per cent</i>			<i>per cent</i>	<i>per cent</i>		
0-13	No well-defined structure	0	Sandy clay loam	Gray, 10 YR 5/1	0.10	1.29	12.9	5.7
13-22		0.1	Sandy clay loam	Grayish brown, 10 YR 5/2	0.08	1.05	13.1	5.6
22-30	Tuff pebbles	34	Sandy loam	Pale brown, 10 YR 6/3	0.04	0.35	8.8	6.1
30-60	Hard tuff con- glomerate	....	.....	Pale brown, 10 YR 6/3	....	....	....	....

The regions near Villavieja, Fortalecilla, and Tello are often described as desert landscapes. On the basis of soil properties and also of rainfall, these areas can hardly be classified as very arid. Natural and man-induced erosion and vegetational exploitation may account for much of the existing barrenness.

*Tropic yellow-brown soils*

On an expedition to the 1-year-old Experiment Station Granja Calima in the heart of the tropical rain forest, extensive areas of yellow soils were encountered. These soils occur on alluvial deposits of Pleistocene age. They are covered with dense vegetation consisting of broad-leaf trees and palms (2). Although leaves seem to be dropping continuously, a well-developed forest floor is absent.

The surface of the ground is incompletely covered with leaves. The humic surface horizon, 1 inch, occasionally 2 inches, deep, is brownish and relatively

high in organic matter. The soil below is uniformly light colored; brilliant yellows predominate. Structural differentiation is absent (table 10).

According to tables 10 and 11 it is surprising to note that yellowish horizons are high in total nitrogen and organic carbon, at least in comparison with the yellow and red soils of southeastern United States. One is reminded of Vageler's statement that "tropical humus substances are colorless" (15).

Several hundred miles north of Granja Calima, but also in the hot, high-rainfall belt, Franco-Urbe has mapped the soils in the vicinity of Urabá, a

TABLE 9  
*Tropic gray-brown soil*  
Neiva profile, No. 62

*Locality:* Neiva (Huila), elevation 470 m. (1,542 feet).

*Climate:* temperature 27.2°C. (81°F.), precipitation 1,239 mm. (41 inches).

*Vegetation:* originally forest (?), now weeds and cacti.

*Topography:* undulating plateau, slope 5 per cent.

*Parent material:* gravel and boulder terrace of middle or late Pleistocene age, predominantly acid igneous material.

*Profile description:*

DEPTH	REMARKS	PARTICLES* > 2 MM.	TEXTURE PARTICLES < 2 MM.	COLOR	N	C	C/N	pH
<i>inches</i>		<i>per cent</i>			<i>per cent</i>	<i>per cent</i>		
0-8	Pebbles, considerably decomposed, friable	52	Fine sandy loam	Brown, 10 YR 5/3	0.19	2.17	11.4	6.5
8-16	Reddish transition zone, related to individual pebbles, friable	40	Fine sandy loam	Yellowish brown, 10 YR 5/4	0.10	0.97	9.7	5.6
16-24		45	Fine sandy loam	Reddish yellow, 7.5 YR 6/6	0.07	0.70	10.0	5.2
24-36		39	Fine sandy loam	Reddish yellow, 7.5 YR 7/6	0.05	0.45	9.0	5.0
36-60	Pebbles larger, less decomposed Relatively fresh boulders	60	Loamy fine sand	Yellow, 10 YR 7/6	0.01	0.24	24.0	6.3

\* Excluding large pebbles.

rubber experiment station. The approximate climatic data are as follows: mean annual temperature 26.7°C. (80°F.), annual precipitation 7,100 mm. (280 inches). The soil types Villa Artega silty clay loam, shallow phase (no. 87), Villa Artega silty clay loam (no. 88), Villa Artega gravelly silty clay loam (no. 90), Río Sucio clay loam (no. 89), and Bejuquillo sandy clay loam (no. 91), contain higher proportions of brown colors, and the surface organic layers have greater magnitudes than those of the yellow soils of the Granja Calima.

Near Villavicencio, in the Llanos, with an annual temperature of 26.3°C. (79°F.) and an annual precipitation of 4,033 mm. (159 inches), yellowish brown



and brown soils occur which might be tentatively assigned to the soils of the tropic yellow-brown group. It should be pointed out, however, that the climate lacks not only extreme humidity, but also uniformity. Two dry seasons alternate with the two wet seasons. In consequence the vegetation is not identical with the typical rain forest. The parent material consists of well-drained Pleistocene alluvial terraces.

In table 11 all samples represent virgin conditions, with the exception of sample 96, which is from a 1-year-old pasture.

TABLE 10

*Yellow soil*

Calima profile, No. 76

*Locality:* Granja Calima, near boundary of Chocó and Valle del Cauca, elevation 30 m. (100 feet).

*Climate:* 1946, temperature 25.6°C. (78°F.), precipitation 8,413 mm. (332 inches).

*Vegetation:* tropical rain forest (broad-leaf trees and palms, dense).

*Topography:* level.

*Parent material:* alluvial terrace (late Pleistocene).

*Profile description:*

DEPTH*	HORIZON DESCRIPTION, TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
-1 to 0	Slightly decomposed leaves, 2.2 tons per acre	Brown, 7.5 YR 5/4	1.75	43.19	24.7	4.7
0 - 2	Humus zone, contains leaf parts, rich in rootlets; sandy loam	Brown, 7.5 YR 5/4	1.03	20.75	20.2	4.6
2 - 8	Many medium-sized roots ( $\frac{1}{4}$ - $\frac{1}{2}$ inch diameter) loam	Light yellowish brown, 10 YR 6/4	0.49	7.20	14.7	5.2
8 -18	Pieces of charcoal; fine sandy loam	Light yellowish brown, 10 YR 6/4	0.39	5.23	13.4	5.4
18 -25+	Sandy clay loam	Pale yellow, 2.5 Y 8/4	0.08	0.87	10.9	5.2

\* Layers above the mineral soil are designated with negative numbers.

*Podzolic yellow soils*

North of the hamlet of Córdoba, near Buenaventura, in the hot per-humid zone of the Pacific lowlands, a podzolic yellow soil (table 12) was observed on a Tertiary, alluvial ridge of 140 m. elevation. This ridge emerges above the plain of yellow soils which consists of Pleistocene deposits. To the observer unfamiliar with plants, the type of forest vegetation appears to be similar on both types of soils.<sup>9</sup> More surprising is the existence of a 4-inch layer of raw humus on the

<sup>9</sup> Cuatrecasas cursorily examined the collected leaves. Over half of them belong to the *Lauraceae*. There were also *Calathea* (a large herb), *Inga* trees (legumes), *Ficus* (an epi-

TABLE 11

*Analytical data of tropic yellow-brown soils*

Region of Granja Calima, No. 75-81; Urabá, No. 87-91; and Villavicencio, No. 95-97

NUMBER	DEPTH	TEXTURE	COLOR	N	C	C/N	pH
	<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
75b	0- $\frac{1}{4}$	Organic loam	Brown, 10 YR 4/3	1.67	38.83	23.3	3.8
75c	$\frac{1}{4}$ - $\frac{3}{4}$	Fine sandy loam	Yellow, 10 YR 7/6	0.20	2.21	11.1	4.6
78	0-8	Very fine sandy loam	Pale yellow, 2.5 Y 7/4	0.19	2.71	14.3	5.1
79a	0-8	Loamy sand	Reddish yellow, 7.5 YR 6/6	0.41	5.54	13.5	6.5
80b	0-42	Organic loam	Yellowish brown, 10 YR 5/4	0.97	13.01	13.4	4.1
80c	$\frac{1}{4}$ - $\frac{3}{4}$	Very fine sandy loam	Yellow, 2.5 Y 8/6	0.20	2.19	11.0	4.7
81b	0-4	Fine sandy loam	Brownish yellow, 10 YR 6/6	0.28	3.24	11.6	4.8
81c	4-8	Fine sandy loam	Yellowish brown, 10 YR 5/6	0.26	2.45	9.42	4.9
87a	0-8	Silty clay loam	Yellowish brown, 10 YR 5/6	0.31	2.11	6.8	5.0
87b	8-24	Gravelly clay loam	Brownish yellow, 10 YR 6/6	0.15	1.18	7.9	5.3
88a	1-8	Silty clay loam	Dark yellowish brown, 10 YR 4/4	0.43	3.42	8.0	5.2
88b	8-22	Silty clay loam	Yellowish brown, 10 YR 5/6	0.22	1.56	7.1	5.1
88c	22-30	Gravelly silty clay loam	Light yellowish brown, 10 YR 6/4	0.13	0.77	6.0	5.3
88d	30-43	Clay loam	Yellow, 10 YR 7/6	0.07	0.12	1.7	5.0
89a	0-4	Clay loam	Pale brown, 10 YR 6/3	0.71	7.48	10.5	5.6
89b	4-12	Clay loam	Brown, 10 YR 5/3	0.40	3.16	7.9	6.1
89c	12-28	Gravelly loam	Light yellowish brown, 10 YR 6/4	0.10	1.19	11.9	5.8
89d	28+	Gravelly loam	Light yellowish brown, 10 YR 6/4	0.05	0.45	9.9	6.0
90a	1-6	Gravelly silty clay loam	Dark grayish brown, 10 YR 3/2	0.78	7.42	9.5	5.8
90b	6-20	Gravelly silty clay loam	Dark yellowish brown, 2.5 Y 4/4	0.27	2.65	9.8	5.9
91a	1-10	Sandy clay loam	Light yellowish brown, 10 YR 6/4	0.29	2.53	8.7	5.5
91b	10-28	Clay loam	Light yellowish brown, 10 YR 6/4	0.06	0.44	7.3	5.4
91c	28-43	Clay loam	Brownish yellow, 10 YR 6/6	0.05	0.39	7.8	5.3
95	0-8	Very fine sandy loam	Yellowish brown, 10 YR 5/4	0.36	4.76	13.2	4.1
96	0-8	Gritty fine sandy loam	Brown, 10 YR 4/3	0.13	1.13	8.7	4.4
97	0-8	Fine sandy loam	Brown, 10 YR 4/3	0.18	3.29	18.3	4.7

podzolic yellow soil, a horizon which is totally lacking on the yellow soils. The light colored A<sub>2</sub> horizon is more than 27 inches thick, but the B horizon was not reached. The area was traversed at the end of a strenuous jungle trip, and the members of the expedition were too tired to explore the profile to greater depth.

#### *Red earths*

In the mountains on the west side of Cauca Valley (Cordillera Occidental) occur very extensive areas of deep, red soils. They are developed on diabase of

TABLE 12

#### *Podzolic yellow soil*

No. 82

*Locality:* near Córdoba, Pacific Coast, elevation 140 m. (460 feet).

*Climate:* estimated, temperature 25–26°C. (77–79°F.), precipitation 5,000–8,000 mm. (200–300 inches).

*Vegetation:* rain forest (broad-leaf trees and palms).

*Topography:* ridge on terrace, slope 2–5 per cent.

*Parent material:* old alluvium, probably Tertiary age, containing quartz pebbles.

#### *Profile description:*

DEPTH*	HORIZON DESCRIPTION	N	C	C/N	pH
<i>inches</i>		<i>per cent</i>	<i>per cent</i>		
–5 to –4	Relatively fresh leaves and branches, 3.1 tons per acre	0.89	48.28	54.1	5.2
–4 to 0	Partly decomposed leaves, 6.8 tons per acre	1.59	47.50	30.0	4.0
0–12	Clay, fine sand, and grit; light gray (10 YR 7/2) with streaks of orange and red	0.13	2.46	18.9	4.6
12–27	Silty clay with some grit; white with patches of yellow-brown	0.03	0.47	15.7	4.6
Nearby 60–84	Yellow and reddish clays				

\* Layers above the mineral soil are designated with negative numbers.

Cretaceous age. Most of the area has been deforested, and erosion has played havoc with the land. Fortunately, a number of forested areas are still intact. In these, only the lower soil horizons, say below 50 inches, are definitely red. The surface soil is dark brown and high in organic matter. It overlies horizons which have a strong yellow component (table 13). In contrast to the uniformly red soils of the Aiken series in California the Colombian red earth profiles having distinct color differentiation should perhaps be designated as podzolized red soils. On the other hand, the light colored horizon of the red earths is yellowish rather than gray, and its thickness exceeds that of North American podzolic profiles manyfold.

Schaufelberger (13) has published an analysis of a red earth near Dagua in the same region. If one calculates molecular ratios, the following values are obtained:

phyte) and *Melastomataceae*. Essentially these leaves correspond to those found on the yellow soils of the Granja Calima.

	Surface soil (humus layer)	Subsoil (red strata)	Rock
$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = \text{sa}$	5.21	2.87	5.02
$\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$	2.04	1.46	2.06
$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{Al}_2\text{O}_3}$	0.168	0.081	0.674
$\beta_1$	0.25	0.12	1
$\frac{\text{CaO} + \text{MgO}}{\text{Al}_2\text{O}_3}$	0.331	0.170	1.70
$\beta_2$	0.19	0.10	1

TABLE 13

Red earth

No. 14

*Locality:* kilometer 18 on road from Cali to Dagua, elevation 1,940 m. (6,365 feet).

*Climate:* estimated, annual temperature 20°C. (68°F.), precipitation 1,500 to more than 2,000 mm. (60 to more than 80 inches).

*Vegetation:* luxuriant broad-leaf forest.

*Topography:* mountainous, slope 10-15 per cent.

*Parent material:* diabase rock of Cretaceous age.

*Profile description:*

DEPTH	PROFILE DESCRIPTION	DEPTH OF SAMPLES ANALYZED	TEXTURE	COLOR	N	C	C/N	pH
<i>inches</i>		<i>inches</i>			<i>per cent</i>	<i>per cent</i>		
0-12	Dark brown fine sandy loam, granular	0-8	Fine sandy loam	Brown, 10 YR 5/3	0.71	10.22	14.4	5.0
12-15	Transition zone of humus							
15-40	Yellowish brown clay loam	34-36	Clay and sand	Brownish yellow 10 YR 6/6	0.13	2.24	17.2	5.7
40-50	Pale yellow clay loam							
50-55	Transition zone reddish							
55-70	Reddish loam	70-72	Clay loam	Reddish yellow, 7.5 YR 6/6	0.02	0.36	18.0	4.9
70-80	Red clay loam							
80-100+	Reddish with yellow stains and white spots	100-102	Sandy clay	Reddish yellow 5 YR 6/8	0.03	0.19	6.3	5.0

Whereas the leaching values  $\beta_1$  and  $\beta_2$  correspond to those of lateritic soils (6), the behavior of silica and the sesquioxides is at variance, since the  $sa$  values suggest a tendency toward podzolization. More analytical work, especially on the clay fraction, will have to be done before definite conclusions can be drawn. Red strata suggesting lateritic material were also observed near Risaralda where they are covered with volcanic ash. Between Pereira and La Virginia, volcanic ash rests on reddish alluvial material. Near Neiva, deep, red sediments are exposed. In the Llanos mottled clays suggesting lateritic strata were observed in a quarry below Pleistocene gravels.

The area of red soils comprises a wide climatic range, both as to temperature and moisture (see figure 3).

#### *Claypan soils*

Soils with heavy B horizons corresponding to the North American claypan soils were encountered near Bogotá, above Cali, at Salado, near Espinal, and between Villavicencio and Pt. López.

Colombian claypan soils tend to be lower in total nitrogen and lighter in color than the adjoining nonclaypan soils. The columnar, blocky aggregates of the B horizon are coated with manganese stains. In general, Colombian claypan soils appear more strongly developed than the Grundy and Putnam series in Missouri or the Tierra series in California. The soils are now treeless and presumably were so when the Spaniards arrived in the middle of the sixteenth century. The climates comprise a considerable range, including the cool, relatively dry one of Bogotá and the humid wet one of the Llanos. From the viewpoint of soil genesis, the most characteristic common feature is the type and age of the parent material, which consists of shales, sandstones, and alluvial material of Tertiary age. Presumably these soils developed during most of the Pleistocene; in other words, their characteristic claypan features are probably conditioned by age and not by topography, as is commonly assumed.

#### *Hardpan soils*

On the high gravel plateaus between Neiva and Baraya in the upper Magdalena Valley hardpan soils were encountered. These soils are very low in organic matter (less than 0.05 per cent total nitrogen). The color of the surface soil is brownish gray. The yellow hardpan was encountered at a depth of about 30 inches, and it is from 15 to 30 inches thick. The present vegetation is xerophytic, but the soils are acid, pH 5.3-5.9.

#### *Rendzinas*

On the steep mountain slopes in the vicinity of Quipile, Cundianamarca, are found dark colored soils derived from shales containing lime seams. The Colombian Soil Survey has mapped these soils as Villeta series and classified them as rendzina. The profiles which the writer examined appear, indeed, identical with rendzina soils in Central Europe.

ZONAL ASPECTS OF COLOMBIAN SOILS<sup>10</sup>

The one feature that most impresses North American pedologists is the strong yellow component in the color of Colombian soils. When the yellow is concealed in the surface soil by dark humus substances, as is often the case, it reveals itself the more vividly in the subsoil.

The blacks and yellows are zonal features. They are related to climate and vegetation. The climatic factor is especially strong in the areal distribution of the black color associated with humus. Yellow color, most conspicuous in the uniformly wet zones, may in part be determined by parent material and time, since certain combinations of rocks and old age are known to produce gray and red colors.

In the hot lowlands, at annual temperatures above 25°C. (77°F.), the tropic gray-brown soils and the tropic yellow-brown soils are members of a *moisture sequence* or *hygrosequence* (fig. 3). Dark humus colors are lacking, and acidity tends to increase from the drier to the wetter regions. The desert-like soils of the Guajira Peninsula, mentioned by Lafaurie (8), presumably constitute the arid member of the sequence. The coordination may be envisaged as follows:

tropic desert soils → tropic gray-brown soils → ? → tropic yellow-brown soils  
(Guajira)

Changes in elevation create clearcut *temperature sequences*. For the precipitation range 1,000–2,000 mm. (40–80 inches) the following “ladder” or *thermo-sequence* may be conceived (fig. 3):

Cold humus soils, and andino podzols  
↑  
Humic yellow-brown soils  
↑  
(Cauca soils)  
↑  
Tropic gray-brown soils

These soil groups are all of Pleistocene age. Their profile differentiation into A and B horizons is not strongly pronounced. The common linkage of the profile features is represented by the dark color and the humus content. Both increase from sea level to mountain ridge.

## THE DILEMMA OF ZONAL AND INTRAZONAL SOILS

In accordance with the aforementioned zonal arrangements, the great soil groups observed in Colombia would align themselves as follows:

<i>Zonal soils</i>	<i>Nonzonal soils (intra-zonal?)</i>
andino podzols	red earths
cold humus soils	podzolized yellow soils
humic yellow-brown soils	giant podzols
(Cauca soils)	clay pan soils
tropic gray-brown soils	rendzinas
tropic yellow-brown soils	

<sup>10</sup> According to the 1938 *Yearbook of Agriculture* (p. 1168), a zonal soil group includes soils having common internal characteristics developed through the influence of environmental forces of broad geographic significance, especially vegetation and climate.



A dilemma is at once apparent. According to conventional procedure, the red earths, the podzolized soils, and the podzols also should be accorded the rank of zonal soils. In Colombia, however, most of the soil groups in the right-hand column are insular and not regional as the definition of a zonal soil would require. If they are of broad geographic significance, like the red earths, they are not zonal in the sense that they are conditioned primarily by climate and vegetation. Parent material and time seem to be the decisive factors. Accordingly the red soils satisfy the definition of intrazonal soils.<sup>11</sup>

The situation is further complicated by the coexistence of conventional zonal soils *in the same climate*. According to figure 3, in the moist subtropical belt, the humic yellow-brown soils, the red earths, and the podzols are climatically closely associated. Likewise, the yellow soils and the podzolic yellow soils of the rain forest possess similar bioclimatic environments. In these areas nature is in discord with the pedologic postulate that different zonal soils should not be coexistent in the same bioclimatic zone.

The position of the claypan soils as intrazonal planosols likewise requires clarification. Rather than topography, old age appears to be the determining cause for the extreme condition of the B horizon. Such a concept is in accord with views expressed by Smith (14).

#### INTERPLAY OF SOIL-FORMING FACTORS

The coexistence of conventional zonal soils in similar climates becomes plausible if one takes into consideration the factors time and parent material.

In North America and in Europe many of the classic zonal soils such as podzols, chernozems, and gray-brown podzolic soils are more or less restricted to areas that were greatly influenced by the ice age. The soils are of Pleistocene and post-Pleistocene age. In equatorial regions glaciation has been a minor factor in soil development. Weathering and soil formation have probably taken place without interruption throughout the Pleistocene and possibly throughout the Tertiary period.

In table 14 an attempt has been made to portray the interplay of present climate, age of soil, and parent material which is responsible for the peculiar soil conditions existing in Colombia. It is assumed that the red earths owe their characteristics not only to climate but more so to age and possibly the nature of the rock. In his elaborate treatise on the geology and soils of Colombia, Schau-felberger (13) has very emphatically stressed the time factor in the development of these soils. Podzols and podzolic soils of the subtropic and tropic regions and also the claypan soils are younger than the red soils but older than the humic yellow-brown soils and the tropic gray-brown and yellow-brown soils. It is not yet clear what conditions are conducive to the genesis of subtropical podzols, on the one hand, or of claypan soils, on the other.

<sup>11</sup> According to the 1938 *Yearbook of Agriculture*: "Any of the great groups of soils with more or less well-developed characteristics that reflect the dominating influence of some local factor of relief, parent material, or age over the normal effect of the climate and vegetation."

The concept of soil sequences (7) offers a solution to the problem of soil classification. The various great soil groups may be compared to playing cards that may be arranged in various orders or sequences. As ordering criteria, one might select internal soil properties (*s*-values) or factors of soil formation. If the latter alternative is chosen, comparable great soil groups may be arranged in climo-sequences, as already suggested, or in chronosequences, as indicated by Smith for the Illinoian claypan soils. In this manner each great soil group is linked systematically to other great soil groups.

TABLE 14  
*Colombian great soil groups related to climate, parent material, and time of soil formation*

PRESENT PERIOD	PLEISTOCENE PERIOD	TERTIARY PERIOD
A. <i>Humid cold climate, &lt;12°C.</i>		
Andino podzols ←	{ volcanic tuff	
Cold humus soils ←		
B. <i>Humid temperature and sub-tropical climate, 16-24°C.</i>		
Red earth ←		diabase
Giant podzol ←		sandstone
Claypans ←		unconsolidated sediments
Humic yellow-brown soils ←	volcanic ash and others	
Cauca soils ←	alluvial material	
C. <i>Humid tropical climate, &gt;25°C.</i>		
Podzolic yellow soil ←		alluvial terraces
Yellow soil (Calima) ←	alluvial terraces	

#### SUMMARY

The climates of Colombia, S. A., and the United States are compared on the basis of "climatic fields." Colombia has a wider range in annual temperature and especially in annual precipitation than the United States.

The following great soil groups are described and are mapped in the climatic field: cold humus soils, podzols, humic yellow-brown soils, Cauca Valley soils, tropic gray-brown soils, tropic yellow-brown soils, red earths, claypan soils, hardpan soils, and rendzinas.

Classifications of Colombian great soil groups according to zonal and intra-zonal soils leads to conflicts with their accepted definitions.

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# STRUCTURE IN BLACK COTTON SOILS OF THE NIZAMSAGAR PROJECT AREA, HYDERABAD STATE, INDIA

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Structure, a vital morphological characteristic of soil, pertains to the arrangement of soil particles into aggregates and defines the architectural form of the profile. Structure determines all circulation within the soil and the penetration of roots. Its influence on plant nutrition, which directly affects crop production, is great.

Joffe<sup>2</sup> has reviewed the work done in Germany, Russia, England, and the United States of America and has explained the dependence on structure of the circulation of moisture in soil, the absorption of water by soils, and the chemical, physical, and biological properties of soil.

The Soil Science Committee of the Indian Council of Agricultural Research, India, has summarized as follows<sup>3</sup> the systems of classification of structure in vogue:

Four systems of classification of soil structure are in common use. Classification of structure according to the Russian and Oxford systems is confined to a description of the shape and size of the structural elements. The categoric names used to define structure according to the American system may or may not include a description of consistence in addition to that of the shape and size of the aggregates. Stremme's classification is based on considerations of shape, porosity, root penetration, permeability of water, and fracture, not much attention being paid to the size of the aggregates. An important item of classification which is common to all the systems is the shape or form of the structural elements. In the Russian, American, and Oxford systems three fundamental forms are recognized: cube- or, sphere-like; column- or, prism-like; and plate-like. The Oxford system introduces an additional form, polyhedral. In Stremme's system the fundamental forms are: round; angular (which includes cubes, polygons, and prisms); and platy. An item of classification which is common to the Russian, American, and Oxford systems but is lacking in Stremme's system is the size of the aggregates.

The Committee, however, felt the lack of greater attention to the study of structure in soils in India. In its recommendation, it urged the need for an intensive study of structure in soil surveys conducted in the country.

## STUDIES ON SOIL STRUCTURE

In 1931 to 1934, observations of soil structure were made by the senior author when he undertook a soil survey of Raichur District to determine the irrigability

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<sup>2</sup> Joffe, J. S. *Pedology*. Rutgers University Press, New Brunswick, N. J. 1936.

<sup>3</sup> Proceedings of the Soil Science Committee of the Indian Council of Agricultural Research, India. Classification of soil structure. February, 1944.

of the soils.<sup>4</sup> From 1943, this study was continued in the survey of soils in the Nizamsagar Irrigation Project. An intensive study of the structure of different soil types, as sandy loams, sandy clays, and clays and clay loams, yielded the following conclusions:

*Sandy loams (red soils)*

In the shallow phase of this soil type, the surface soil is generally granular and sometimes fluffy. The texture is increasingly coarse with depth to the underlying disintegrating rock material. The subsoils are usually hard and massive, the hardness increasing with depth.

In the deep phases of this type, the clay content increases with depth. If the soil is of the normal type, the subsoil exhibits nutty to cloddy structure. If alkaline, the soil in this horizon is compact and hard and of prismatic columnar structure. Below it, is the hard massive disintegrating parent rock.

*Black soils*

Black soils consist of sandy clays, clay loams, and clays.

In the surface soil the structure is granular to crumbly, whereas in the sub-surface from a depth of 3 or 4 to 6 or 8 inches it is laminated or fine platy.

The structure in subsoils is nutty to fragmental cloddy and then cloddy to blocky with increasing depth to about 3 feet.

In alkaline soils, prismatic to columnar structure is seen, with the top of the columns rather flat.

In the deeper soils, the subsoil reveals a distinctive structure. This structure has been termed *lentil*, as it bears a close resemblance to the lentil seed, which has the shape of a double-convex lens. This structure was observed earlier in the Raichur District and mentioned in the soil survey report of the Tungabhadra project area. It was also observed, about the same time, by Ramiah and his assistants<sup>5</sup> in the Bellary District when the Tungabhadra Project area on the Madras side was surveyed. Similar structural pattern was reported by Ellis,<sup>6</sup> who termed it *diagonally platy*. But the structural pattern termed *lentil* does not seem to have been studied in detail.

The lentil is a unique structure found in subsoils of the black cotton soils in granitoid gneissic areas. The Nizamsagar Central Development Board of H.E.H. the Nizam's Government financed a study of the black soils of this tract with a view to their efficient utilization for irrigation cultivation. Because of the great importance of soil structure and its influence on the movement of moisture in soils, a detailed study was undertaken and field observations were made for several seasons. The results are embodied in this paper.

<sup>4</sup> Mehta, J. B. Report on the Agricultural Survey, Tungabhadra Project, Raichur District. 1932.

<sup>5</sup> Ramiah, P. V. 1934-1935 Soil Survey Report, Tungabhadra Project Area, Madras Presidency.

<sup>6</sup> Ellis, J. H. The Soils of Manitoba. Manitoba Economic Survey Board. 1938.

## THE LENTIL STRUCTURE

Vast stretches of normal clays and clay loams in the Nizamsagar area possess a singular, well-defined structure, which, after critical study in the field, has been termed *lentic*.

In soils where this structure is feebly developed, only the upper part of each aggregate is well defined, presenting a convex lens shape. This is termed *convex lentic*. Where the structure is well developed, the aggregate has a double-convex

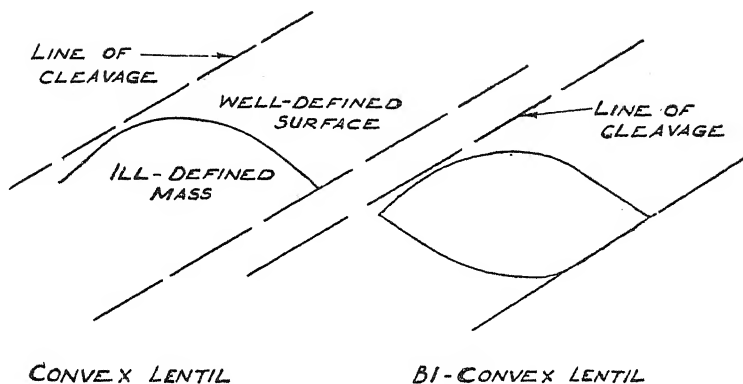


FIG. 1. CONVEX LENTIC AND BI-CONVEX LENTIC STRUCTURES

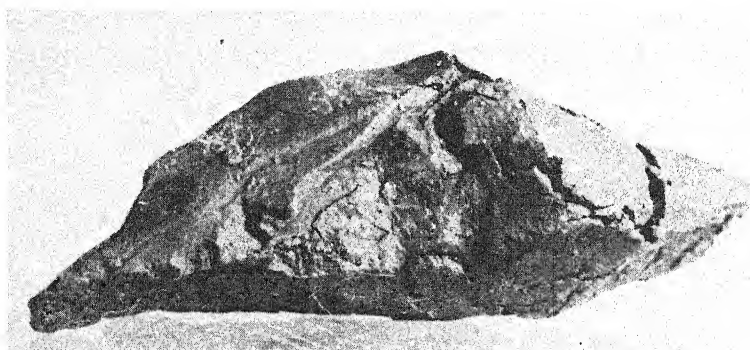


FIG. 2. CHARACTERISTIC BI-CONVEX LENTIC AGGREGATE

lens shape and is termed *bi-convex lentic*. These structures are illustrated in figures 1 and 2.

The lentils vary greatly in size in the different textured soils. They are usually 7 by 4 inches, 8 by 5 inches, and 9 by 5 inches and can be detached one by one with ease from the huge lentils in the soil body. They are stable and not easily shattered. These aggregates are seen to glomerate into larger lentils of similar shape, several feet in length and width, fitting in with the depth of the lentic horizon as illustrated in figure 3.

In some profiles, the inside of the aggregates is of one color, and the outside is of a different color or has a glossy coating. This indicates that concentration or precipitation is taking place in this horizon and denotes movement of material into it from above or from below. Sometimes the lentils present a dull appearance, denoting, perhaps, removal of material *from* that horizon by leaching.<sup>7</sup>

The smaller aggregates of 7 by 4, 8 by 5, and 9 by 5 inches are seen clearly as the moisture evaporates and the cleavage planes form distinctly. In soils with

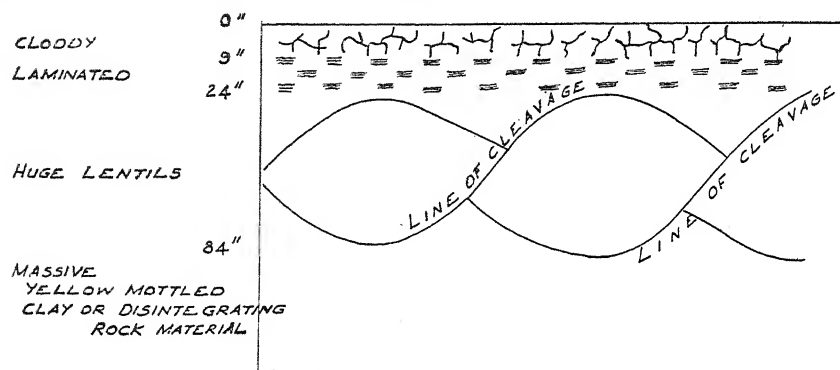


FIG. 3. CHARACTERISTIC ARRANGEMENT OF LENTIL AGGREGATES IN THE SUBSOIL

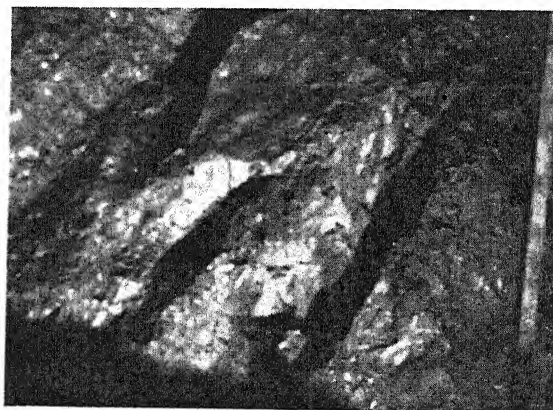


FIG. 4. PARALLEL CLEAVAGE PLANES OF LENTIL STRUCTURE

impeded drainage, these smaller aggregates are faintly visible or indistinguishable and, where distinguishable, they cannot be peeled off into further small lentils. They are seen to break up into hard irregular or prismatic fragments. In soils with good subsoil drainage, the lentils are soft and peel off into several similar very small stable lentils measuring 1 by  $\frac{1}{4}$  inch.

Within the soil profile, the size of the lentils increases with increasing depth. But this structure becomes less pronounced, as the moist, massive, yellowish or brownish mottled horizon is approached at lower depths, to 5 or more feet.

<sup>7</sup> See footnote 6.



The cleaving consists of a set of parallel planes inclined to the ground surface, dipping toward the fall of the land (figs. 4 and 5). Fresh profiles when exposed soon after cessation of the monsoonic period exhibit only a few major planes of cleavage, which indicates that water permeates freely through these structural

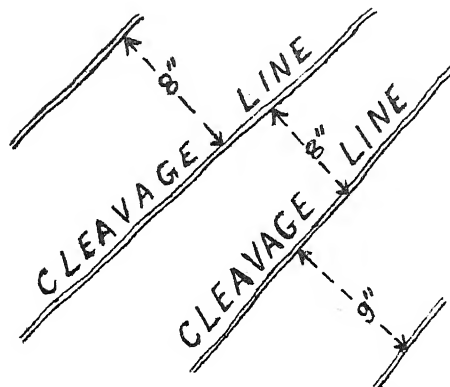


FIG. 5. CLEAVAGE PATTERN OF FIGURE 4

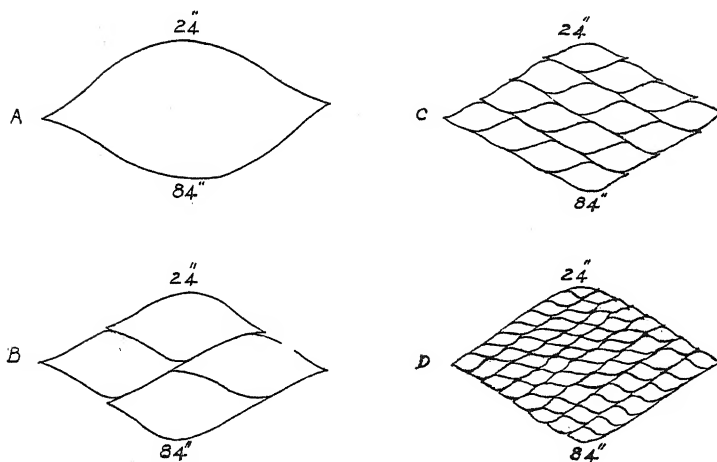


FIG. 6. EFFECT OF DESICCATION ON LENTILS

A. Huge lentils soon after rainy season. B and C. Increasing fragmentation during winter season. D. Final fragmentation during hottest part of summer.

clays in the rainy season. Large quantities of water are absorbed by the subsoil, and the clay swells. In the dry season, because of high temperatures, the soil is desiccated, and further cleaving takes place. In summer, when the temperature is highest, the effect is most pronounced, and the subsoil breaks into innumerable small lentils as a result of their separation from the larger aggregates due to shrinkage. Even at this stage, the large aggregates are clearly discernible as lentils. When further exposed, as in a trench for study, the lentils fall off,

leaving the topsoil intact. This process or fragmentation proceeds with the cessation of rains and is accelerated in summer. Figure 6 shows clearly the effect of desiccation on these huge lentils.

Figure 7, a view, in a trench, of the face lying along the slope of the land, shows the smaller lentils and the glomerated larger lentils all dipping toward the fall of the land.

Figure 8, a view, in a trench, of the face lying against the slope of the land, shows the structural pattern, consisting of a number of small bi-convex lines of cleavage, which clearly represent the cross sections of the smaller lentils.

The structural pattern in the opposite faces of any trench are similar. The cleaving, as seen in two faces of a trench, at right angles to each other, is shown in figure 9.

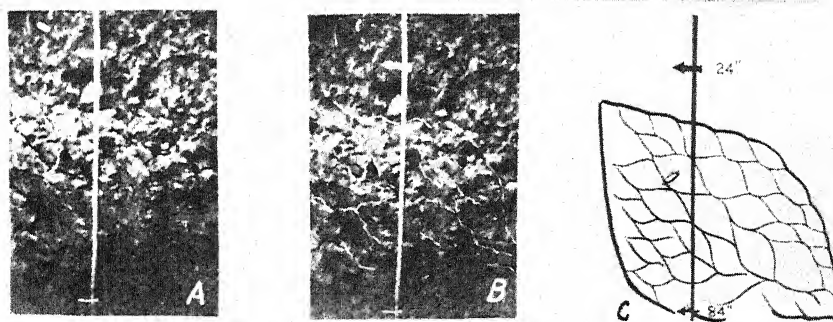


FIG. 7. BI-CONVEX LENTIL STRUCTURE IN A TRENCH-FACE LYING ALONG THE SLOPE OF THE LAND

A. View of the trench-face. B. Some of the cleavage planes in A emphasized by cotton stuffing in the cracks. C. Sketch of the cleavage pattern.

#### LENTIL STRUCTURE IN RELATION TO CERTAIN SOIL CHARACTERISTICS

The richest soils encountered in the Nizamsagar project area are the clays in which the lentil structure is well defined. The soils have good tilth. Their high absorption and good subsoil drainage have made sheet erosion negligible and gully formation scarcely noticeable.

The process of fragmentation of the large lentils with desiccation possibly helps in the rapid recuperation of these soils, resulting in their high productivity. This problem is being studied separately by the Soil Research Section.

Alkaline patches are rare in soils of this structure. Effective percolation of rain water and its seepage to the natural drainageways probably prevent accumulation of alkali salts in these deep black soils. Even nodular lime formation is scarcely noticeable above the moist, massive, yellowish brown mottled horizon at a depth of 6 or more feet.

#### FORMATION OF LENTIL STRUCTURE

The Nizamsagar tract lies between  $77^{\circ}44'$  and  $78^{\circ}25'$  east longitudes, and  $18^{\circ}13'$  and  $19^{\circ}01'$  north latitudes. It comprises an area of 631,000 acres (fig. 10).

The southern part is hilly and very undulating. The rest of the tract is gently undulating to sloping. The river Manjra-Godavari forms the boundary, and the land has a good fall toward the river border northward.

The tract is in a belt of hot and humid tropical climate with wet and dry seasons, where rainfall exceeds evaporation.

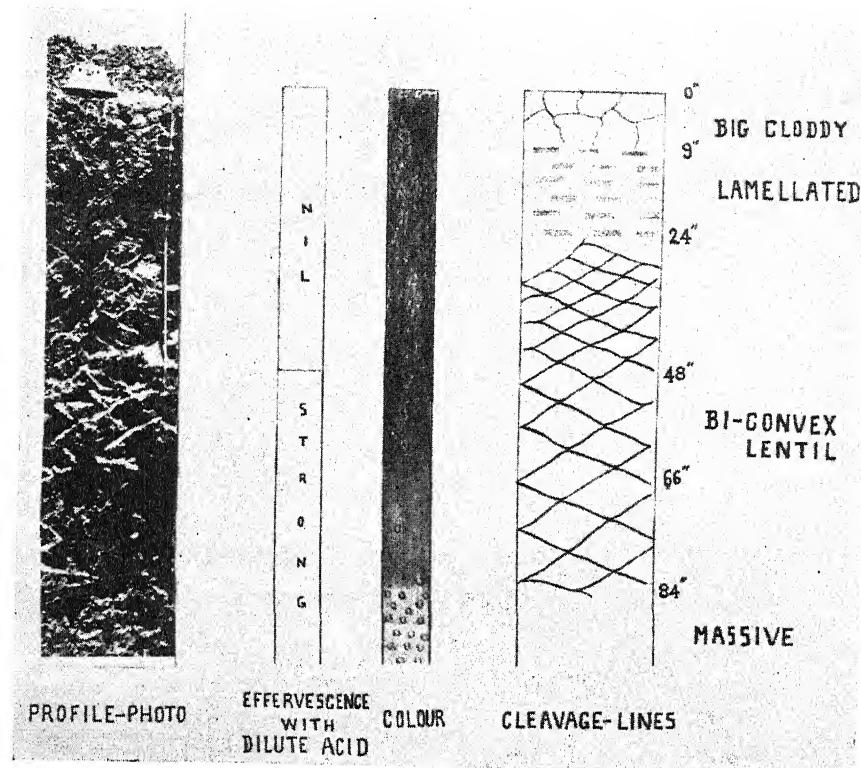


FIG. 8. BI-CONVEX LENTIL STRUCTURE IN A TRENCH-FACE LYING AGAINST THE SLOPE OF THE LAND

Survey 60/1 in the Nizamsagar project area: Pegadpally village, Bodhan taluq, Nizamabad district, Hyderabad (Deccan) state.

The natural vegetation consists of the forest-steppe type—forest vegetation in red soils and steppe type in the black soils.

In the granitoid-gneissic hilly areas, sandy loams predominate, with patches of sandy clay and clays in the deep depressions and valley slopes. In the lower reaches of hills, sandy clays are encountered. Still farther down are the deep black clay soils, stretching to the river border. This clay region has a network of natural drainage basins.

The clays in the sandy loam region and its vicinity have impeded drainage. The subsoil water table in them is usually high, about 5 to 7 feet from the ground level. The high water table in these impeded clays and the numerous ponds formed in the depressions tend to keep them constantly damp and humid.

The river-border clays are thoroughly drained and are markedly permeable. The subsoil water table in them is very low, 14 or more feet from the ground level. It is in these clays with good subsoil drainage that the lentil structure is well exhibited.

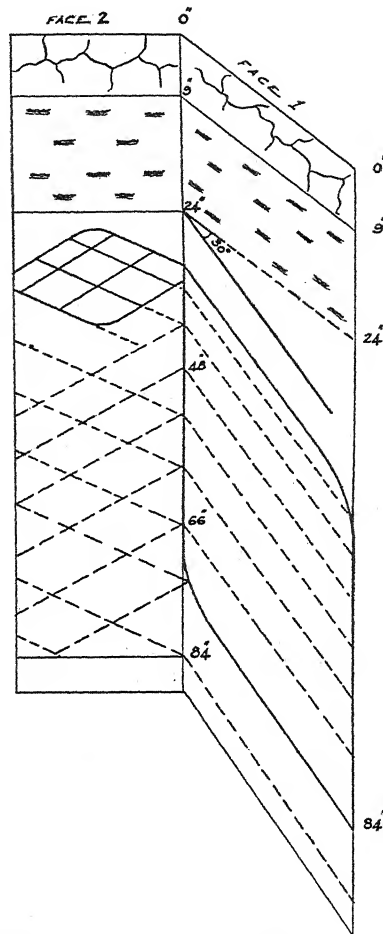


FIG. 9. CLEAVAGE IN TWO FACES OF A TRENCH AT RIGHT ANGLES TO EACH OTHER:  
FACE 1 LYING ALONG THE SLOPE OF THE LAND, AND  
FACE 2, AGAINST THE SLOPE

The movement of water through the subsoil seems to be in a direction slanting to the fall of the land. This is the resultant of two forces, one along the slope of the land and the other in the gravitational direction. Because of this type of movement inclined parallel planes of cleavage are formed (see figures 4 and 5). The general dip of these cleavage planes seems to be around  $30^\circ$ .

In the impeded clays, these parallel planes of cleavage are few and far between and not so distinct. Toward the river border, as the gradient increases, the

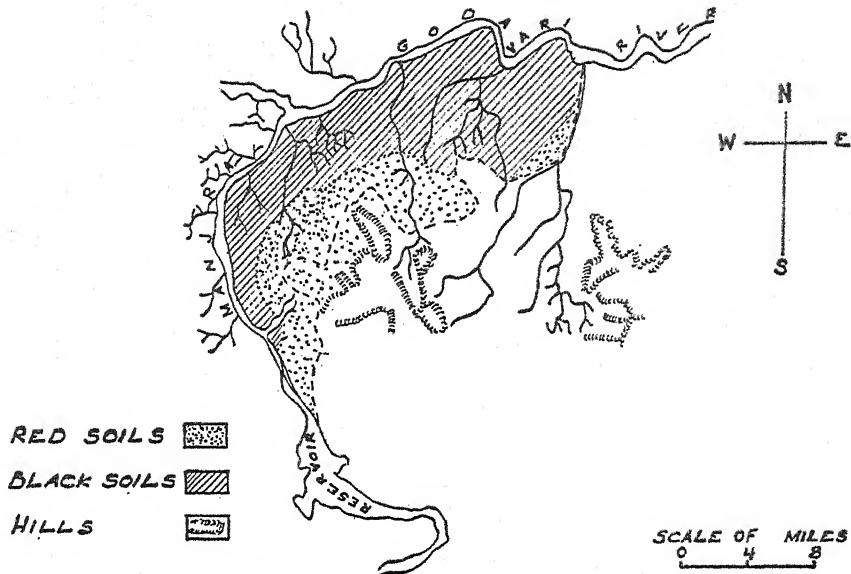


FIG. 10. SOIL MAP OF NIZAMSAGAR PROJECT

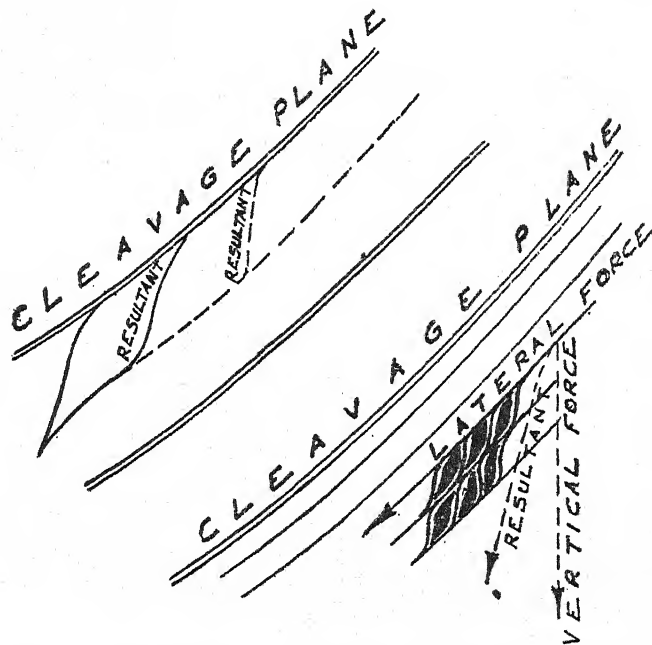


FIG. 11. CLEAVAGE PLANES IN LENTICULAR-STRUCTURED BLACK SOILS

subsoil drainage improves, and the cleavage planes become numerous and more distinct.



As these planes of cleavage become well defined, the movement of water along them is accelerated. There is a simultaneous formation of a number of oblique planes of cleavage, the resultant of the lateral and vertical forces, yielding the lentil-structured pattern in the black soils. This is illustrated diagrammatically in figure 11.

#### CONCLUSION

Fairly good slope of land, free subsoil drainage, and high permeability of the river-border clays seem to favor the lentil type of structural formation.

The lentil structure helps percolation, prevents runoff, and controls erosion. Clays with this structure are highly productive. This may be due to prevention of accumulation of alkali salts and free upward movement of soil solution, containing valuable plant-food material, toward the root zone of the cultivated plants during the crop seasons. Because of the free drainage in such soils the water table is considerably lower than in the other types.

#### SUMMARY

The deep black soils studied in the Nizamsagar area exhibit a characteristic structure in their subsoil. This structure was observed in the Raichur District in 1931. From 1943 this structure has been studied in the Nizamsagar project area under the soil survey scheme financed by the Nizamsagar Central Development Board.

The shape, size, and makeup of the structural aggregates do not fit into any of the commonly recognized forms, as cube or spherelike, columnar or prismatic, and platy. The structure is termed *lentil*, as it closely resembles the lentil seed.

When the structure is feebly developed, only the upper surface of the aggregate is convex-lens shaped; when well developed, the aggregate is bi-convex lens shaped.

The lentils are stable and measure 7 by 4 inches, 8 by 5 inches, and 9 by 5 inches. They can be detached with ease from the soil body. In soils with impeded drainage the lentils are feebly developed and are hard. These break into irregular or prismatic clods. In good, pervious soils they are not so hard and peel off into several similar-shaped very small lentils measuring 1 by  $\frac{1}{4}$  inch.

The lentil aggregates form parts of huge similar-shaped lentils, several feet in length and width, fitting in with the depth of this structural horizon.

The structural pattern consists of a set of parallel planes of cleavage inclined about  $30^\circ$  to the ground surface and in the direction of subsoil drainage.

Soils possessing this characteristic lentil structure are highly productive, highly absorptive, and not easily erodible. Alkaline patches are few.

# UTILIZATION OF NITROGEN IN CROPPING SYSTEMS WITH AND WITHOUT GREEN MANURE IN THE GREENHOUSE

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The value of green manure crops in maintaining soil organic matter, thereby improving the physical condition of the soil and providing for a steady release of plant nutrients, is well recognized. Under some conditions these green crops may be grown as catch or cover crops, utilizing soil nitrogen that would otherwise be lost in large part in the drainage water. Under other conditions, however, the soil nitrogen supply may be so inadequate that only a meager growth of the green crop is obtained unless fertilizer nitrogen is supplied to it. Is it advisable to add nitrogen in such cases, or would it be preferable to apply all of the nitrogen directly to a growing major crop, and thus increase the immediate money return? Aside from purely economic factors, the answer to this question is dependent in large part upon (a) the extent to which soil organic matter can be maintained, or increased, by the regular turning under of green crops of various stages of maturity, (b) the rate of release of nitrogen from such added organic matter, and (c) the ultimate fate of the added nitrogen, particularly whether a portion escapes to the atmosphere. The present report gives the results of a long-time greenhouse experiment that was planned to furnish information upon the points mentioned. This experiment is somewhat similar to the one reported previously (3, 6).

## EXPERIMENTAL PLAN AND METHODS

The general plan of the experiment was to grow a green crop to various stages of maturity and then, after turning this under, to plant an indicator crop. Nitrogen, supplied in the form of urea, was added to both the green crop and the indicator crop at varying rates. The total additions of phosphorus and potassium were the same for all pots; where a green crop was grown, a portion was added to this crop and the remainder to the indicator crop. This process of growing a green crop and then an indicator crop was repeated five times, and then the soils were allowed to remain fallow at optimum moisture content for 1 year. They were analyzed initially for total nitrogen and carbon and finally for nitrogen, carbon, and nitrates. The dry weights and nitrogen contents of all indicator crops were obtained. All treatments were made in triplicate, but one of these was used for estimating the quantity of carbon that was added to the soil in the green crop. The data in the tables are averages of two replications.

The experiments were conducted in the greenhouse in 2-gallon glazed pots con-

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taining 20 pounds of Evesboro loamy sand obtained from near Beltsville, Maryland. The soil was limed to pH 6 before the experiment was started and once during the experiment so as to maintain the reaction at approximately this level. Details of the cropping and fertilizer treatments are summarized in table 1. Four of the green manure crops were millet and one was rye; the indicator crops were three of Sudan grass and two of wheat. The quantities of phosphorus and potash used may seem high, but this soil is especially deficient in phosphorus, and in the greenhouse, crops frequently show signs of phosphorus deficiency where the application is below 300 pounds of  $P_2O_5$  per acre (2,000,000 pounds of soil).

The green manure crops were turned under at three stages of maturity, namely, (a) 10 to 12 inches in height, (b) at the heading stage, and (c) at maturity. They were cut up while green and mixed with all of the soil in the various pots.

The indicator crops, which were harvested when the heads were forming, were dried, ground, and analyzed for total nitrogen, including nitrates, by the Kjeldahl method. The roots were left in the soil and broken up during the process of mixing the green manures and fertilizers with the soil prior to planting of the next crop.

#### EXPERIMENTAL RESULTS

##### *Crop yields*

The average yields of dry matter for the five successive indicator crops are given in table 2. These data show that, on the basis of total added nitrogen, the yields were always higher where the nitrogen was all added to the indicator crop rather than a portion to produce the green crop. This is as expected, since any nitrogen added in the green crop is, in large part, unavailable for the crop that follows. In general, the results show that the more mature the green crop, the greater the decrease in yields per unit of total nitrogen applied. This is due not so much to the maturity of the green crops as to the larger amount of carbon produced by the more mature crop and added to the soil. All of these results agree closely with the earlier experiment (3, 6). Both the intermediate and the mature green crops, when added without nitrogen other than that used in producing them, depressed the yields of the indicator crops below the controls. The depressing effect increased with the maturity of the plant material added.

The response of the indicator crops to added nitrogen was nearly linear, except where the added green crop did not contain enough nitrogen for complete decomposition. When this deficiency was satisfied the yields were then approximately linear.

##### *Nitrogen recovery*

The average recoveries of nitrogen by the five indicator crops are given in table 3 and in figure 1. In all cases the percentage nitrogen recovery by a particular crop is calculated on the basis of total nitrogen added to the green crop immediately preceding and to the indicator crop.

The recoveries of added nitrogen show a decrease with increase in the maturity

TABLE 1  
*Time of planting and harvesting and fertilizer additions,  
 other than nitrogen, made to various crops*

CROP NUMBER	KIND OF CROP	DATE OF		TREATMENT	
		Planting	Harvest*	CaCO <sub>3</sub> lb./A.	Fertilizer† lb./A.
1	<i>Green manure crops</i> Millet	(a) June 21, 1943 (b) July 12, 1943 (c) Aug. 2, 1943	Aug. 17, 1943 Aug. 19, 1943 Aug. 23, 1943	1500	1200
3	Rye	(a) Dec. 20, 1943 (b) Jan. 31, 1944 (c) Mar. 20, 1944	Apr. 26, 1944 Apr. 26, 1944 Apr. 26, 1944	....	1000
5	Millet	(a) Aug. 9, 1944 (b) Sept. 6, 1944 (c) Oct. 6, 1944	Oct. 18, 1944 Oct. 26, 1944 Nov. 6, 1944	....	1000
7	Millet	(a) Mar. 12, 1945 (b) Apr. 18, 1945 (c) May 23, 1945	June 19, 1945 June 19, 1945 June 19, 1945	....	1335
9	Millet	(a) Aug. 28, 1945 (b) Sept. 28, 1945 (c) Oct. 31, 1945	Nov. 1, 1945 Nov. 21, 1945 Dec. 15, 1945	....	1335
2	<i>Indicator crops</i> Sudan grass	Sept. 13, 1943	Nov. 16, 1943	....	(x) 1800 (y) 3000
4	Sudan grass	May 19, 1944	July 7, 1944	1000	(x) 1000 (y) 2000
6	Wheat	Oct. 18, 1944	Feb. 26, 1945	....	(x) 1335 (y) 2335
8	Sudan grass	July 2, 1945	Aug. 21, 1945	....	(x) 1335 (y) 2670
10	Wheat	Dec. 19, 1945	Apr. 8, 1946	....	(x) 1335 (y) 2670

\* Whenever green manures were harvested at different dates the crops were kept in a cold storage room until ready to be mixed with the soil.

† The fertilizer used was a 0-12-8 for the first green manure crop and for the first indicator crop; the others received a 0-15-6 mixture.

(a) = Green manure crop grown to maturity.

(b) = Green manure crop grown to intermediate stage.

(c) = Green manure crop grown to young stage.

(x) = Fertilizer added to pots on which green manure crops were grown.

(y) = Fertilizer added to pots where no green crop was grown. The applications are such as to make the total additions to all pots the same, regardless of the presence or absence of the green crop.

of the green crop. The larger yields produced where the green crop was allowed to grow for a longer time resulted, of course, in a larger amount of carbon being

added to the soil. Furthermore, the carbon-nitrogen ratio increased with maturity beyond the critical 35 to 1 ratio (4), and this meant that a part of the nitrogen, added after the green crop was turned under, was used to decompose the

TABLE 2  
Average yields of dry matter from five successive indicator crops

AGE OF GREEN CROP	UREA N ADDED PER CROP TO		1ST CROP*	2ND CROP*	3RD CROP†	4TH CROP*	5TH CROP†	FIVE CROPS	INCREASE OVER CHECK
	Green crop	Indicator crop							
	lbs./A.	lbs./A.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
None	0	0	17.6	10.8	2.9	7.4	2.3	41.0	.....
		40	25.6	30.6	10.1	31.8	9.2	107.3	66.3
		60	26.9	39.4	13.9	38.9	12.3	131.4	90.4
		80	28.1	46.1	18.9	50.3	17.8	161.2	120.2
		100	25.6	52.4	20.2	57.6	19.7	175.5	134.5
		120	26.1	55.3	23.0	57.0	23.6	185.0	144.0
Mature	40	160	34.3	62.2	29.8	70.8	28.6	225.7	184.7
		0	1.0	5.2	1.5	5.0	2.5	15.2	-25.8
		20	2.3	9.5	2.1	9.8	5.3	29.0	-12.0
		40	3.5	14.2	3.3	16.7	7.1	44.8	3.8
Intermediate	40	80	15.0	30.1	7.0	29.7	15.9	97.7	56.7
		0	2.1	7.5	2.0	6.3	5.6	23.5	-17.5
		20	5.4	15.1	4.7	13.2	7.5	45.9	4.9
		40	8.8	25.1	6.4	17.0	10.5	67.8	26.8
Young	40	80	16.1	39.7	13.7	35.7	18.6	123.8	82.8
		0	10.7	24.5	6.6	11.7	9.9	63.4	22.4
		20	16.9	31.0	10.9	23.0	15.4	97.2	56.2
		40	16.0	38.8	15.3	32.0	14.4	116.5	75.5
Mature	80	80	18.9	52.6	23.3	47.2	27.0	169.0	128.0
		0	1.2	4.9	1.5	7.8	3.1	18.5	-22.5
		20	2.0	5.6	2.4	9.5	5.8	25.3	-15.7
		40	4.7	9.5	2.8	14.3	8.7	40.0	-1.0
Intermediate	80	80	14.5	26.5	7.1	30.4	16.6	95.1	54.1
		0	5.1	8.7	4.4	5.2	8.3	31.7	-9.3
		20	7.5	11.9	8.6	16.9	12.8	57.7	16.7
		40	11.1	25.4	10.4	27.9	19.4	94.2	53.2
Young	80	80	15.1	39.8	17.8	38.6	28.8	140.1	99.1
		0	16.8	34.9	14.0	24.5	15.6	105.8	64.8
		20	19.4	44.6	20.4	36.8	20.0	141.2	100.2
		40	18.3	52.1	23.0	44.0	25.5	162.9	121.9
		80	18.8	57.6	29.0	53.8	29.6	188.8	147.8

\* Sudan grass.

† Wheat.

added organic material rather than for growth of the indicator crop. In case of the intermediate and mature green crops, recovery of added nitrogen in the first indicator crop was either negligible or a negative value. Subsequent indicator



crops showed slightly higher values due to some release of nitrogen from the earlier crops, but the values for the last indicator crops varied only between 15 and 32 per cent for the soils where the two more mature crops were added. The

TABLE 3  
*Average recoveries of nitrogen by five indicator crops*

AGE OF GREEN CROP	UREA N ADDED PER CROP TO		PER CENT OF ADDED N RECOVERED IN					
	Green crop	Indicator crop	1st crop*	2nd crop*	3rd crop†	4th crop*	5th crop†	Five crops
	lbs./A.	lbs./A.						
None	0	0	.....	.....	.....	.....	.....	.....
		40	47.4	46.9	39.2	46.9	29.2	41.9
		60	48.9	47.8	44.1	49.3	28.3	43.7
		80	41.9	49.9	51.0	50.7	36.4	46.0
		100	46.1	48.8	49.6	45.4	34.2	44.8
		120	43.0	46.1	47.8	40.8	38.4	43.2
Mature	40	160	37.9	52.1	51.2	46.5	36.7	44.9
		0	-46.9	-7.7	-6.1	1.7	9.4	-9.9
		20	-27.9	1.1	-0.7	8.5	15.4	-0.7
		40	-19.0	5.5	3.0	12.7	16.3	3.7
		80	1.1	18.4	11.4	19.7	25.2	15.1
Interme- diate	40	0	-43.0	-0.6	0.6	3.9	21.0	-3.9
		20	-18.4	8.8	10.3	11.4	20.2	6.5
		40	-3.0	19.3	11.6	12.1	21.8	12.2
		80	12.9	28.1	23.3	19.9	31.3	23.1
Young	40	0	9.4	25.9	20.4	9.9	38.6	20.8
		20	25.7	30.5	33.1	25.4	40.1	31.0
		40	32.0	39.2	40.8	23.7	31.2	33.4
		80	30.9	44.9	50.0	37.3	41.6	40.9
Mature	80	0	-23.2	-3.9	-3.9	3.0	6.3	-4.3
		20	-17.0	-2.2	-1.1	5.7	9.9	-0.9
		40	-11.2	1.3	2.2	8.3	14.7	3.1
		80	1.9	10.5	7.6	14.2	23.0	11.4
Interme- diate	80	0	-15.2	1.4	6.1	1.9	17.9	2.4
		20	-8.8	3.3	14.8	9.5	25.4	8.8
		40	-1.1	13.2	16.9	16.4	33.5	15.8
		80	16.5	22.2	29.8	27.0	41.2	27.4
Young	80	0	27.9	31.7	34.7	17.4	33.6	29.1
		20	38.8	34.4	45.9	21.0	35.3	35.1
		40	34.7	42.1	44.2	29.6	40.8	38.3
		80	36.3	49.0	55.3	34.3	44.8	43.9

\* Sudan grass.

† Wheat.

growth of the young green crop lowered recoveries to some extent below the control, but the decrease was not marked because the quantity of carbon added in the green crop was small.

The comparative nitrogen recoveries where 40 and 80 pounds of nitrogen per green crop was added (fig. 1) show no very marked differences. The extra nitrogen slightly increased the average percentage recovery of nitrogen where the young and intermediate green crops were grown, and slightly decreased it where the green crop grew to maturity. In general, the extra nitrogen merely produced more green crop, which inactivated more nitrogen, with a final resulting low nitrogen recovery except with the young crop, where doubtless not all of the nitrogen added to the green crop was utilized by it.

It is rather surprising that even where no green crop was added the average nitrogen recovery in the indicator crops was under 50 per cent for all crops, and

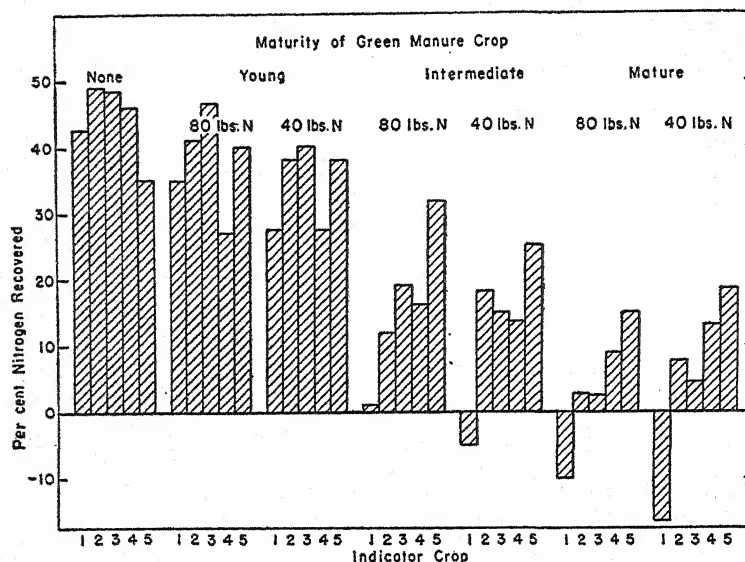


FIG. 1. RECOVERY OF NITROGEN BY FIVE SUCCESSIVE INDICATOR CROPS RECEIVING UREA, A PORTION OF WHICH WAS USED FOR GROWING GREEN MANURE CROPS TO DIFFERENT STAGES OF MATURITY

Results for various rates of urea averaged

that the values for the last crops were no higher than for the first. Where the mature green crop was added, there was some increase in nitrogen recovery with time, as already pointed out, but the increase was small.

#### *Soil humus formation and nitrogen availability*

After the fifth indicator crop was harvested, all of the soils were mixed thoroughly and were maintained in the greenhouse at optimum moisture content for 1 year. They received one additional mixing at the end of the first 6 months of fallowing. At the end of the year they were again mixed and sampled for analysis. Table 4 gives the final soil carbon, total nitrogen and nitrate contents, as well as the calculated carbon-nitrogen ratios of the total soil organic matter and of the organic matter formed during the experiment.

In calculating the carbon-nitrogen ratio of the soil organic matter, the nitrate nitrogen values found at the end of the fallow period were first subtracted from the total nitrogen values. The carbon-nitrogen ratio of the organic matter

TABLE 4

*Average carbon and nitrogen contents of variously treated soils after 10 successive crops*

AGE OF GREEN CROP	TOTAL N ADDED TO ALL CROPS	FINAL SOIL C*	GAIN IN SOIL C	GAIN IN SOIL C	FINAL SOIL N†			FINAL C/N RATIO OF SOIL ORGANIC MATTER‡	C/N RATIO OF ORGANIC MATTER FORMED IN SOIL
					Total	Nitrate	Total less nitrate		
	lbs./A.	tons/A.	tons/A.	%	lbs./A.	lbs./A.	lbs./A.		
None	0	6.10	-0.14	-2.2	598	16	582	21.1	....
	200	6.55	0.31	4.7	684	19	665	19.7	10.8
	300	6.70	0.46	7.4	723	23	700	19.1	10.2
	400	7.10	0.86	13.8	771	28	743	19.1	12.4
	500	7.50	1.26	20.2	800	27	773	19.4	14.7
	600	7.60	1.36	21.8	824	37	787	19.3	14.6
Mature	800	7.75	1.51	24.2	858	46	812	19.1	13.0
	200	7.40	1.16	18.6	870	37	833	17.8	10.4
	300	7.70	1.46	23.4	945	43	902	17.0	10.0
	400	7.80	1.56	25.0	975	50	925	16.9	9.9
	600	8.35	2.11	33.8	1044	66	978	17.1	11.4
Interme- diate	200	7.00	0.76	12.2	849	32	817	17.1	7.7
	300	7.30	1.04	16.7	874	38	836	17.5	9.5
	400	7.70	1.46	23.4	892	36	856	18.0	11.7
	600	8.40	2.16	34.6	1013	40	973	17.3	11.8
Young	200	6.45	0.21	3.4	717	24	693	18.6	6.3
	300	6.65	0.41	6.6	805	24	781	17.0	5.5
	400	7.20	0.96	15.4	797	30	767	18.8	11.4
	600	7.45	1.21	19.4	863	46	817	18.2	11.5
Mature	400	8.35	2.11	33.8	958	40	918	18.2	13.4
	500	8.90	2.66	42.6	1046	46	1000	17.8	13.4
	600	8.90	2.66	42.6	1096	52	1045	17.0	12.1
	800	9.65	3.41	54.7	1182	84	1099	17.6	13.7
Interme- diate	400	7.80	1.56	25.0	972	46	927	16.8	9.9
	500	8.25	2.01	32.2	1014	29	985	16.8	10.7
	600	8.05	1.81	29.0	1025	40	986	16.3	9.7
	800	8.60	2.36	38.0	1063	61	1002	17.2	11.7
Young	400	7.10	0.86	13.8	847	46	802	17.7	9.1
	500	7.25	1.01	16.2	870	42	826	17.5	9.3
	600	7.65	1.41	22.6	886	56	832	18.4	12.4
	800	7.85	1.61	25.8	988	60	929	16.9	10.1

\* The carbon content of the original soil was 6.24 tons per acre (2,000,000 pounds of soil).

† The nitrogen content of the original soil was 619 pounds per acre.

‡ The carbon-nitrogen ratio of the original soil was 20.2.

formed in the soil during the experiment was estimated by finding the gain in nitrogen and carbon above that of the check and calculating the ratio from these values.

The data show that the addition of either nitrogen or carbon to the soil increased the quantity of organic matter. This gain, due to nitrogen alone, increased with the quantity of nitrogen added. The maximum gain was 24 per cent. This is a very large value, especially when it is considered that it represents the carbon left after a 4-year experiment, including a year of fallow at the end. This fallow period should have been adequate for nearly complete humification of the plant-root residues previously mixed with the soil.

Where green crops were added, the maximum gain in soil carbon was 54 per cent. This occurred where the largest mature green crop was added. Intermediate stage green manure produced the next largest gains, and the youngest material the least. These comparative figures apparently reflect the total quantity of carbon added more than the maturity of the green crop and crop residues.

The apparent carbon-nitrogen ratio of the soil organic matter formed in the soil averaged about 9.4 for the young crop, 10.2 for the intermediate crop, 11.8 for the mature crop, and 12.6 for no green crop. These values are in the same order as those reported in another experiment (3, 6) except that they are about 20 per cent lower. The lower values are probably due primarily to the much longer duration of the present experiment, which would permit more complete humification.

All green manure and nitrogen treatments lowered the carbon-nitrogen ratio of the soil. The original value for the untreated soil was 20.2, whereas at the time of the final analysis the ratios varied between 16.3 and 19.7. Even the addition of the mature green crop lowered the carbon-nitrogen ratio of this particular soil. Probably an important factor was the increase in oxidation of the soil organic matter brought about by addition of the fresh energy sources, as reported by Broadbent and Norman (1).

The nitrate accumulation figures in table 4 were, in general, highest where the lowest recoveries in nitrogen in the indicator crops were obtained, showing that the nitrogen that was inactivated by the added carbon was being released. The quantities of nitrate formed were not, however, proportional to that previously inactivated, but were comparatively small where the intermediate and mature green crops were added. Presumably in these cases either the more mature materials were slower to decay and release their nitrogen, or else the carbon-nitrogen ratio merely remained high and thus slowed down the rate of nitrogen release. The latter factor appeared to be the more important. It should also be noted that where considerable nitrogen, but no green crop, was added, the nitrate production was approximately twice that in the controls that received no nitrogen. The soils that received only urea did, of course, have considerable carbon added to them in the form of root residues from the indicator crops. These residues, which consisted of roots from plants harvested at the time the heads were forming, seem to have decomposed nearly as rapidly as the young green manure crops. From similar results reported elsewhere (6), it may be said that the response of the crop, if one had been planted at the time the nitrate analyses were made, would undoubtedly have been similar to the nitrate accumulation values.

The percentages of the total added carbon that remained in the soils at the end of the 4-year experiment can be calculated with a fair degree of accuracy. The

TABLE 5

*Effect of additions of green manures of various stages of maturity on accumulation of carbon in a cropped greenhouse soil*

TREATMENT-TOTALS FOR 5 INDICATOR CROPS*			CARBON ADDED IN GREEN CROP	CARBON ADDED IN ROOTS OF IN- DICATOR CROPS†	APPROX. TOTAL C ADDED		FINAL SOIL C‡	INCREASE IN SOIL CARBON		
Age of green crop	Urea N added to green crop	Urea N added to in- dicator crop			Total	Above control		Total	Per cent of total added C	Av. per cent of total C retained
	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.		
None	0	0	0	1,897	1,897		12,200			
		200	0	4,963	4,963	3,066	13,100	900	29.4	
		300	0	6,078	6,078	4,181	13,400	1,200	28.7	
		400	0	7,456	7,456	5,559	14,200	2,000	36.0	
		500	0	8,118	8,118	6,221	15,000	2,800	45.0	
		600	0	8,557	8,557	6,660	15,200	3,000	45.0	
Mature	200	800	0	10,440	10,440	8,543	15,500	3,300	38.6	37.1
		0	17,100	703	17,803	15,906	14,800	2,600	16.3	
		100	17,100	1,341	18,441	16,544	15,400	3,200	19.3	
		200	17,100	2,240	19,340	17,443	15,600	3,400	19.5	
		400	17,100	4,519	21,619	19,722	16,700	4,500	22.8	19.5
Interme- diate	200	0	12,400	1,087	13,487	11,590	14,000	1,800	15.5	
		100	12,400	2,123	14,523	12,626	14,600	2,400	19.0	
		200	12,400	3,136	15,536	13,639	15,400	3,200	23.5	
		400	12,400	5,726	18,126	16,229	16,800	4,600	28.3	21.6
Young	200	0	3,450	2,933	6,383	4,486	12,900	700	15.6	
		100	3,450	4,496	7,946	6,049	13,300	1,100	18.2	
		200	3,450	5,389	8,839	6,942	14,400	2,200	31.7	
		400	3,450	7,817	11,267	9,370	14,900	2,700	28.8	23.6
Mature	400	0	25,250	856	26,106	24,309	16,700	4,500	18.5	
		100	25,250	1,170	26,420	24,523	17,800	5,600	22.8	
		200	25,250	1,850	27,100	25,203	17,800	5,600	22.2	
		400	25,250	4,399	29,649	27,752	19,300	7,100	25.6	22.3
Interme- diate	400	0	17,250	1,585	18,835	16,938	15,600	3,400	20.1	
		100	17,250	2,669	19,919	18,022	16,500	4,300	23.9	
		200	17,250	4,357	21,607	19,710	16,100	3,900	19.6	
		400	17,250	6,480	23,730	21,833	17,200	5,000	22.9	21.7
Young	400	0	4,450	5,290	9,740	7,843	14,200	2,000	25.5	
		100	4,450	6,531	10,981	9,084	14,500	2,300	25.3	
		200	4,450	7,535	11,985	10,088	15,300	3,100	30.7	
		400	4,450	8,733	13,183	11,286	15,700	3,500	31.0	28.1

\* Three crops of Sudan grass and two of wheat.

† Estimates are based upon the assumptions that one-third of the total dry weight of the plants was in the roots, and that they contained 42 per cent carbon.

‡ The original soil contained 12,480 pounds of carbon per acre (2,000,000 pounds of soil).

additions include the carbon in the five green crops plus that added in the root residues of the five indicator crops. The carbon in the green crops was de-



terminated directly, as already explained. The carbon in the roots was estimated by assuming that a third of the total dry weight of the plants was in the roots. This is approximately correct, as already shown (5). The percentages of this

TABLE 6  
*Soil nitrogen balance sheet*

AGE OF GREEN CROP	TOTAL N ADDED TO ALL CROPS	ORIGINAL SOIL N PLUS ADDITIONS	N REMOVED IN 5 CROPS	FIN L SOIL N	TOTAL N RECOVERED	N GAIN OR LOSS
	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.	lbs./A.
None	0	619	51	598	649	+30
	200	819	134	684	818	-1
	300	919	182	723	905	-14
	400	1019	235	771	1006	-13
	500	1119	274	800	1074	-45
	600	1219	310	824	1134	-85
	800	1419	410	858	1268	-151
Mature	200	819	31	870	901	+82
	300	919	49	945	994	+75
	400	1019	66	975	1041	+22
	600	1219	142	1044	1186	-33
Intermediate	200	819	43	849	892	+73
	300	919	70	874	944	+25
	400	1019	100	892	992	-27
	600	1219	189	1013	1202	-17
Young	200	819	92	717	809	-10
	300	919	144	805	949	+30
	400	1019	184	797	981	-38
	600	1219	296	863	1159	-60
Mature	400	1019	34	958	992	-27
	500	1119	49	1046	1095	-24
	600	1219	70	1096	1166	-53
	800	1419	142	1182	1324	-95
Intermediate	400	1019	61	972	1033	+14
	500	1119	95	1014	1109	-10
	600	1219	145	1025	1170	-49
	800	1419	270	1063	1333	-86
Young	400	1019	168	847	1015	-4
	500	1119	226	870	1096	-23
	600	1219	280	887	1167	-52
	800	1419	402	988	1390	-29

added carbon that remained as soil humus are shown in the last column of table 5.

The average carbon retention figures were for mature green crop 20.9, intermediate green crop 21.7, young green crop 25.9, and no green crop 37.1 per cent. In interpreting these figures it must be borne in mind that the percentages of added carbon derived from the green crops and from the indicator crops varied

widely. In the case of both the mature and intermediate green crops the yields of the indicator crops were so depressed that a much smaller proportion of the total added carbon came from the root residues than from the green crop. On the other hand, where the young green crop was added, usually more of the carbon came from the roots of the indicator crops than from the green manures. In view of these facts, the figures given above would seem to indicate that under the experimental conditions there was no marked difference between the carbon retention in the form of humus whether derived from a young or a mature green crop. The comparatively high value for the carbon added exclusively as roots was probably due in part to the resistance of the fibrous roots to decay, and even more to the fact that during most of the time that they were decomposing almost no available nitrogen was present to hasten the rate of decay.

#### *Gains and losses of soil nitrogen*

A nitrogen balance sheet for all of the treatments is shown in table 6.

The number of treatments in which losses occurred was greater than those in which gains occurred (23 vs. 8). In general the more nitrogen added, the greater the loss. The variations were between a gain of 82 and a loss of 151 pounds of nitrogen per acre during the experimental period. As was to be expected, the gains usually occurred where the carbon-nitrogen ratio of the organic matter was wide. Some of the apparent gains were due to nitrogen added in the tap water, which contained an average of about 0.5 p.p.m. of total nitrogen. This corresponds to an addition of about 15 to 30 pounds per acre during the period of the experiment. The quantity of water added, of course, varied with the amount of plant growth.

When the nitrogen added in the tap water is disregarded, the average net loss of nitrogen for all 31 treatments was 4.2 per cent of that supplied; if an average of 20 pounds of nitrogen per acre was added in the tap water, the loss was 8.7 per cent. These results agree closely with those from a similar previous experiment (6).

#### DISCUSSION

One of the most striking facts brought out by this experiment is that added carbon was retained in the soil more tenaciously than might have been expected. Paralleling this retention of carbon was a retention of nitrogen corresponding to a carbon-nitrogen ratio of near 10 or higher. The net result, therefore, of the addition of urea nitrogen to soils to produce green manure crops was to fix a large percentage of the added nitrogen so that it was not recovered in the indicator crops during the experiment. In some cases the net recovery of nitrogen was zero. The yields of successive crops, and the final soil nitrate determinations after a year of fallow, show that the nitrogen was being released, but only slowly.

Even where no green crop was grown, less than 50 per cent of the nitrogen applied to the indicator crops was recovered in the harvested portions of these crops. Since only about a third of the weight of the plants was in the roots, it may seem surprising that over half the nitrogen was retained in the soil and roots.

At least three factors may be involved: First, the roots have a comparatively wide carbon-nitrogen ratio, and hence not only is their nitrogen slow to be released during decomposition but this nitrogen-deficient organic matter may inactivate other nitrogen added subsequently. Second, the soil used had an initial carbon-nitrogen ratio of 20.2 and it may have also inactivated some of the urea nitrogen. Third, the soil colloids may have fixed some of the ammonium ion, as Joffe and Levine (2) and others have shown. Although the tendency of additions of nitrogen alone to maintain (or increase) soil organic matter is undoubtedly overemphasized in this greenhouse experiment, it does seem that the practical importance of this fact has been emphasized too little in the past. The present experiment, which agrees with the previous one (3, 6), suggests that it is possible under some soil and climatic conditions to maintain soil organic matter at a reasonably satisfactory level by using abundant fertilizer nitrogen on crops that produce large yields of dry matter and have extensive root systems. Crops such as grasses that require little or no stirring of the soil should be most effective.

The age of the green crop added had little effect on the percentage of the carbon retained. In other words, the experiment indicates that succulent green manure carbon and mature green manure carbon are retained to nearly the same extent. The data are not, however, adequate to show this with a high degree of accuracy, for the reason that green manure carbon was never added alone but always together with the root residues from the various indicator crops. It seems certain, however, that the maturity of the green crop was of much less importance than the quantity of carbon added.

The nitrogen balance sheet also brings out some important practical results. In this experiment, where there was no leaching, most of the added nitrogen could be accounted for in the crops and in the accumulated organic matter. Gaseous losses of nitrogen did not seem to be of great importance. Likewise, abundant added energy sources did not cause much bacterial nitrogen fixation from the atmosphere.

It is a well-known fact that, in the fertilization of crops with commercial nitrogen, if the nitrogen is not utilized by the crop to which it is applied there is likely to be only a small crop response the second year. The reasons for this have never been fully understood. Loss of nitrogen in the drainage water has been emphasized, and justly so. The present experiment shows that it is also possible for much of the nitrogen to remain in the soil in the form of soil organic matter or partly decomposed plant roots and other crop residues.

One of the purposes of the experiment reported here was to determine how long a period is required for the nitrogen recoveries in the indicator crops, grown after the green manure additions, to equal or surpass those from crops grown in the absence of green crops. The experiment shows that after five indicator crops the nitrogen recoveries were still much higher in the absence of the mature and intermediate green crops; where the young crop was turned under, the values differed very little from those of the treatment with nitrogen alone. The experiment covered a period of about 3 years of continuous cropping and almost continuous additions of root carbon that delayed decay by keeping the level of available

nitrogen low. Under field conditions the time factor would be different, fewer crops per year would be grown, and any cultivation or fallowing would tend to accelerate decay and release of nitrogen.

Although the present greenhouse experiment overemphasizes the ease with which soil organic matter can be maintained or increased, the principles involved are well illustrated. These principles, which are not new, are (a) to add as much carbon as possible, together with sufficient nitrogen to form humus, and (b) to keep the soil in a crop with as little cultivation as possible. It may seldom be practical, or advisable, to attempt to build up soil organic matter but, if consideration is given to the main factors involved, the level of organic matter can be kept at a reasonably adequate level. The proportion, if any, of the nitrogen that should be applied to the green crop, rather than to the main crop, will vary with the soil, climate, and crop.

#### SUMMARY

The results of a 4-year greenhouse experiment designed to study the utilization of urea nitrogen in cropping systems with and without green manure are reported. The effects of the additions of nitrogen, and of green manures and root carbon, on soil organic matter content are also given. The main results were as follows:

1. The largest yields and highest recoveries of nitrogen in the crop were obtained where no green crops were turned under; these values decreased with increase in maturity of the green crop.

2. Even in the absence of green crops less than half of the added nitrogen was recovered in the five indicator crops. The remainder was used to produce soil organic matter.

3. The comparative nitrogen recoveries in the indicator crops, where 40 and 80 pounds of nitrogen were used to grow the green crops, showed no marked differences. The extra nitrogen merely produced more green crop and thus inactivated more nitrogen except where the green crop was turned under while very young and before it had used all the nitrogen.

4. The nitrogen inactivated by the carbon (green manure nitrogen) was only slowly released to subsequent crops. Where the two more mature green crops were added, the nitrogen recovery in the fifth indicator crop was less than where no green crop was grown, regardless of the large additions to the previous five green crops and four indicator crops.

5. Soil analysis showed that the addition of nitrogen alone to the soil increased the quantity of soil carbon. At the end of the 4-year experiment the gains from the root residues increased with added nitrogen to a high of 24 per cent.

6. The gains in soil carbon where green crops were added were as much as 54 per cent with the mature green crop and less for the more succulent crops. The important factor was the quantity of carbon added.

7. The apparent average carbon-nitrogen ratios of the humus formed were 9.4, 10.2, 11.8 and 12.6 for the young, intermediate, and mature green crops, and for no green crop, respectively.

8. Nitrate analyses of the soil at the end of the experiment following a year of



fallow gave the highest values where the lowest recoveries of nitrogen in the crop had been obtained.

9. The percentages of the carbon added as green manures and roots that remained in the soils at the end of the experiment were approximately 20.9, 21.7, 25.9, and 37.1 for the mature, intermediate, and young green crops, and no green crop, respectively.

10. The nitrogen balance sheet shows slight gains of nitrogen where materials of wide carbon-nitrogen ratios were added, but for other treatments some losses, usually less than 10 per cent of that added, were found.

11. It is emphasized that the large increases in soil carbon reported here could not be expected to be obtained under field conditions, but the principles involved should have rather general application.

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# TESTING SOILS FOR LIME REQUIREMENT BY MEANS OF A BUFFERED SOLUTION AND THE GLASS ELECTRODE<sup>1</sup>

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The pH is one of the best single-value measurements of the condition of a soil with respect to lime. The exchangeable hydrogen content of soil is one of the best measures of the amount of ground limestone required by lime-deficient soils.

By combining use of the glass electrode and the concept of depression of the pH of a buffered solution as a measure of exchangeable hydrogen, first introduced by Brown (1), testing of soils for lime requirement becomes a relatively simple and adequately accurate determination.

This paper is devoted to the development of a method for rapid determination of the lime requirement of a deficient soil based on the depression of the pH of a buffered solution. The theory and design of a desirable type of buffered solution for the purpose indicated and a detailed description of a satisfactory procedure and some results obtained with the method are presented.

The basic concept for determination of the lime requirement of soil involves the use of a solution buffered at pH 7 and of such a character that the pH of the mixture of soil and solution decreases linearly with respect to the exchangeable hydrogen content of the soil. If the buffering capacity of such a solution is large with respect to that of the soil added to the solution, and if the depression of the pH of the solution is restricted to small values, then the depression of the pH of the mixture of soil and solution approaches an absolute measure of the amount of exchangeable hydrogen in the soil. The following properties of such a buffered solution are also desirable:

A combination of chemical substances should be chosen that does not react unfavorably with the soil.

A rapid rate of reaction is desirable.

The results should not be affected appreciably by the nature of the soil.

The depression in pH should be in a convenient ratio to the hydrogen content of the soil.

The above conditions have been approached closely in a mixture of calcium acetate, *p*-nitrophenol, and magnesium oxide. The cations in this system, namely, calcium and magnesium, are the dominant basic ions present in soil. They may be combined in approximately the same ratio as that in soil. The acetate and nitrophenol salts of these cations are soluble and there is no undesirable reaction between the anions of these salts and soil.

<sup>1</sup> Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Journal Series No. 1100.

<sup>2</sup> Instructor in soils.



THEORY AND DESIGN OF A BUFFERED SOLUTION FOR MEASURING SOIL  
LIME REQUIREMENT*Characteristics of the titration curves of calcium acetate and paranitrophenol*

The buffering capacity of a solution of calcium acetate as determined from a titration curve varies smoothly from a high value at pH 6 to a low value at pH 7. Conversely, the buffering capacity of *p*-nitrophenol varies smoothly from a low value at pH 6 to a high value at pH 7. Over this range of pH values, any desired shape of titration curve from concave through linear to convex may be obtained by decreasing the proportion of acetate to *p*-nitrophenol. These properties provide a buffered solution ideally suited to the problem under consideration.

*Rate of reaction*

The relatively high rate of reaction that is desirable in a test for lime requirement based upon the quantity of exchangeable hydrogen in the soil depends upon injection, into the insoluble, negatively charged clay system, of a soluble salt in sufficient quantities to bring out the hydrogen associated with the clay. Potassium chloride provides an excellent unbuffered neutral salt for this purpose. The salts of calcium acetate and *p*-nitrophenol serve the same function in a highly buffered system.

The change in pH with respect to time of a mixture of 10-mesh soil and a buffered solution used according to the procedure described in a later paragraph was investigated to determine the minimum time required to establish a constant pH level. The mixture of soil, water, and solution was stirred thoroughly for 30 seconds after the solution was added and again for 30 seconds before the pH reading of the mixture was taken. Different samples were used for the different intervals of time so that the amount of stirring each sample received did not vary.

The results showed that, for an easily dispersed silt loam, equilibrium was established within 16 minutes after the solution was added to the soil. The change in pH of a well-aggregated clay soil at the end of 16 minutes was 90 per cent of the value attained at the end of 210 minutes. The reactions between soils and solution were so nearly complete at the end of 16 minutes that a period of 15 to 30 minutes was established as adequate for testing soils. The slowness with which the clay soil reached equilibrium appeared to be caused by failure of the clay to disperse. Thorough stirring to obtain dispersion rather than a constant time of stirring is suggested.

*Properties of the exchange complex of soil*

The original concept of use of the depression of the pH of a buffered solution as a measure of exchangeable hydrogen in soil assumes that the buffering capacity of the solution will be high with respect to that of the soil. To ensure sufficient depression of the pH for accurate and convenient measurement, the buffering capacity of the solution in contact with the soil must not, however, be too great. The buffering capacity of the soil itself must also be considered.

The buffering capacity of different clay minerals was investigated to determine applicability of the method to soils of widely different mineral composition. Increments of NaOH were added to successive flasks of electrolyzed clay in the presence of the unbuffered neutral salt KCl. The titration curves are shown in figure 1. They have been plotted with the assumption that in the presence of the unbuffered salt the clays are 100 per cent saturated with bases at pH 7. This is in fair agreement with results reported by Mitra (3) for titration curves

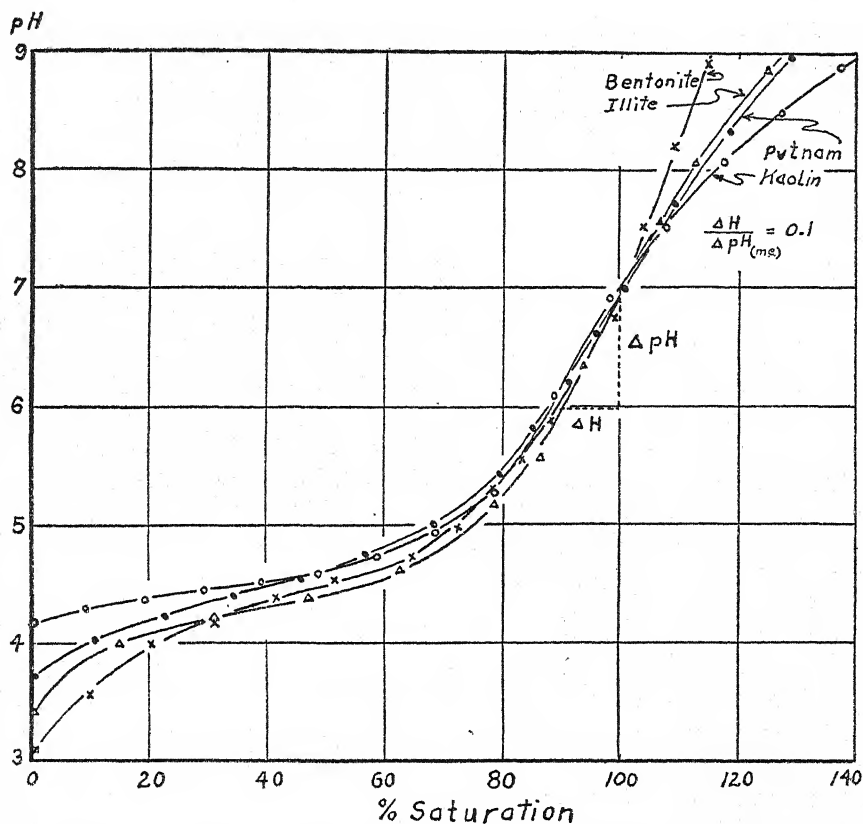


FIG. 1. TITRATION CURVES OF DIFFERENT CLAYS IN PRESENCE OF KCl

obtained with  $\text{Ca}(\text{OH})_2$  in the absence of a salt, which is considered the most representative measure of the amount of lime required to neutralize a soil.

The slopes of the titration curves over the range from pH 6 to pH 7 are essentially uniform and the same for the different clay minerals. The results reported by Mitra for the titration of clay with different cations also show that buffering capacities of clay are not affected materially by the cation used. Since, in the method under consideration, the buffering capacity of the clay is of secondary importance to the buffering capacity of the solution added to the clay, the effects of the cations used play only a third order rôle, which may be neglected.

The buffering capacity of the clay may be expressed as the milliequivalents of

hydrogen required to change 1 m.e. of clay 1 pH unit in the vicinity of neutrality. The results taken from the curves of figure 1 indicate that a buffering capacity of 0.1 m.e. of hydrogen per milliequivalent of exchange capacity will describe soil adequately for purposes of the method under consideration.

*Relation of depression of pH to exchangeable hydrogen content of soil*

Choice of the relation between depression of the pH and exchangeable hydrogen content of the soil is arbitrary. Use of a strongly buffered solution which restricts depression of the pH to small values, reduces variations caused by differences in the exchange capacity of the soil, but requires very accurate determinations of the pH of the system. Use of a moderately buffered solution, with proper allowances for the buffering capacity of the soil, results in greater depressions of the pH which can be measured with conventional equipment without too much sacrifice in accuracy of the determination from differences in the exchange capacities of the soil.

A depression in pH of 0.1 unit for each milliequivalent of hydrogen in 100 gm. of soil provides a fair compromise of the various factors involved. It may be measured easily with commercial pH equipment. Each tenth of a pH unit then has a calcium carbonate equivalent of 1,000 pounds per acre-plow-depth, thus permitting a reading of soil lime requirement directly from the scale of the pH meter.

The titration curve of the mixture of buffering salts, calcium acetate, and *p*-nitrophenol departs from linearity below pH 6. Because of this, depression of the pH in excess of 1 unit ceases to be a reliable measure of exchangeable hydrogen. Those few soils containing hydrogen in excess of 10 m.e. per 100 gm. may be tested satisfactorily by doubling the amount of solution added to the soil so that each tenth of a unit depression in pH corresponds to 2,000 pounds of limestone per acre.

*Buffering capacity of a solution used with soil for estimating exchangeable hydrogen*

A depression in pH of 0.1 unit for each milliequivalent of hydrogen present in the soil corresponds to a total buffering capacity for the system of 10 m.e. of hydrogen per unit change in pH per 100 gm. of soil. For reliable results, most of this buffering capacity must be supplied by the buffered solution. The fraction of the total buffering capacity supplied by the soil is determined by the exchange capacity of the soil. The majority of soils that need liming may be assumed to be about 50 per cent saturated with bases as a first approximation in the design of the method under consideration. The exchange capacity of these soils will then vary from near 0 to 20 m.e. per 100 gm. for exchangeable hydrogen contents varying from 0 to 10 m.e. per 100 gm. The buffering capacity of such soils, as determined by their exchange capacities and the relations exhibited in figure 1, will vary from 0 to 2.0 m.e. per pH unit per 100 gm. The ideal buffered solution for mixture with soils of this character would be one with a buffering capacity varying from nearly 10 m.e. per pH unit in the vicinity of pH 7 to 8 m.e. per pH unit

in the vicinity of pH 6. A solution approaching these conditions was attained in a mixture of 10 gm. of *p*-nitrophenol and 30 gm. or 0.17 mole of Ca acetate per liter, neutralized to pH 7 with a suitable base such as magnesium oxide. This solution when mixed with 50 per cent base-saturated soil in the ratio of 200 ml. per 100 gm. of soil, produced a combination in which the calculated depression of the pH, as shown in figure 2, followed very closely the desired relation of a depression of 0.1 pH unit for each milliequivalent of hydrogen present in the soil. The linear character of the relation attained in figure 2 is accomplished through

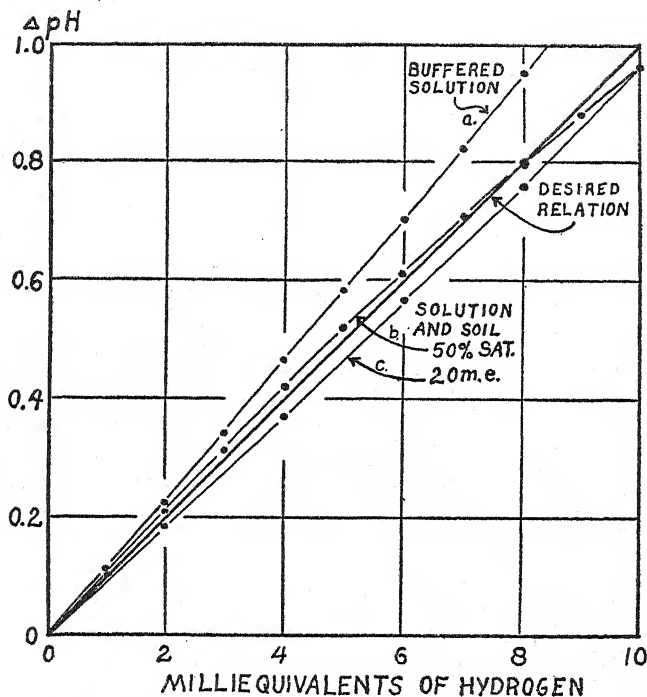


FIG. 2. DEPRESSION OF pH IN RELATION TO QUANTITY OF ACID ADDED TO A BUFFERED SOLUTION DESIGNED TO EXPRESS LIME REQUIREMENT OF SOIL IN TERMS OF FINELY GROUND LIMESTONE

the use of a chemical excess of the *p*-nitrophenol over the calcium acetate to provide a slightly greater buffering capacity at pH 7 than at pH 6.

The depression of the pH in relation to the exchangeable hydrogen has been calculated for a mixture of solution and a soil with a constant exchange capacity of 20 m.e. per 100 gm. These results, shown by the lower curve of figure 2, do not deviate by more than 0.04 pH units from the desired relation of 0.1 unit per milliequivalent of hydrogen. Similar calculations for a hydrogen system would produce a curve between that of the buffered solution alone and that of the soil 50 per cent saturated with bases. It is apparent from these considerations that unless a soil possessed an exceedingly high exchange capacity, a very close estimation of the exchangeable hydrogen content would be obtained from the depres-



sion of the pH of a buffered solution in contact with the soil, on a scale that could be measured satisfactorily by conventional pH instruments.

*Soil lime requirement in relation to depression of pH of a buffered solution*

The concept of liming the soil to a pH level in the vicinity of 6.0 to 6.5 is fairly well established, but simple methods of determining the amount of limestone to add to the soil in order to attain a desirable degree of saturation of the exchange complex with bases have not been available.

The characteristics of the buffered solution exhibited in figure 2 are suited to determination of the lime requirement of a soil where limestone is applied as finely ground or 40-mesh material that reacts readily with the exchange complex of the soil.

When limestone is added at the above rate and mixed throughout the surface 2 million pounds of soil there is assurance that the amount is adequate but not excessive. Although the quantity indicated above is sufficient to bring the soil to pH 7, the heterogeneity of a mixture of soil and limestone brought about by lack of thorough mixing of the soil and presence of some material in the limestone that does not react immediately with the soil provides the needed insurance that the soil will not be completely neutralized.

A number of factors require consideration when 10-mesh mill-run or agricultural lime is used on the soil. Shollenberger and Salter (4) have indicated that about 70 per cent of high-calcium material will become available the first year when it is well mixed with the soil. This material, however, is usually mixed with only the upper layers of soil for the first few years that it is on the land. It does not become mixed throughout the plow depth of soil until the legume crop for which it was applied is plowed under for a succeeding crop. On light-textured soils of low exchange capacity, where the total base content is low, correspondingly greater amounts of lime are required for growth of legumes than on fine-textured soils of high exchange capacity, which contain larger quantities of basic ions. Limestone applied to light-textured soils reacts more readily with the soil than limestone applied to fine-textured soils where the lime does not penetrate many of the aggregates and clods. The object of liming is to raise the degree of saturation of the soil with bases to a reasonable value of 75 to 80 per cent and not to neutralize all of the hydrogen present.

Rather than attempt to evaluate the above factors exactly in order to design a buffered solution for which the depression of the pH was related directly to the lime requirement, a study was made of numerous soils for which the required rate of liming was well established by practice over a period of years. The exchangeable hydrogen content of these soils was measured by direct titration in the presence of KCl. A buffered solution of calcium acetate and *p*-nitrophenol in such proportions as to provide a linear titration curve between pH 6 and pH 7 was adjusted in strength until each 0.1 unit depression of pH occurred for each milliequivalent of hydrogen in the soil. Heavy-textured clay subsoils for which the buffering capacity was high were used to ensure buffering capacity as great as that which might be encountered in the field. The resulting solution possessed



a buffering capacity of 7 m.e. per unit depression of the pH when used in the ratio of 200 ml. per 100 gm. of soil. The titration curve is shown in figure 3. The desired relationships between depression of pH and exchangeable hydrogen content occurred when the solution was used with a soil of 30 m.e. exchange capacity. Also shown as curves in figure 3 are the calculated depressions of the pH of mixtures of the solution with soils one-half and two-thirds saturated with basic ions.

Maximum deviation of the curves for the half saturated soil from the desired relation is slightly over 1 m.e. per 100 gm. of soil. The percentage deviation is

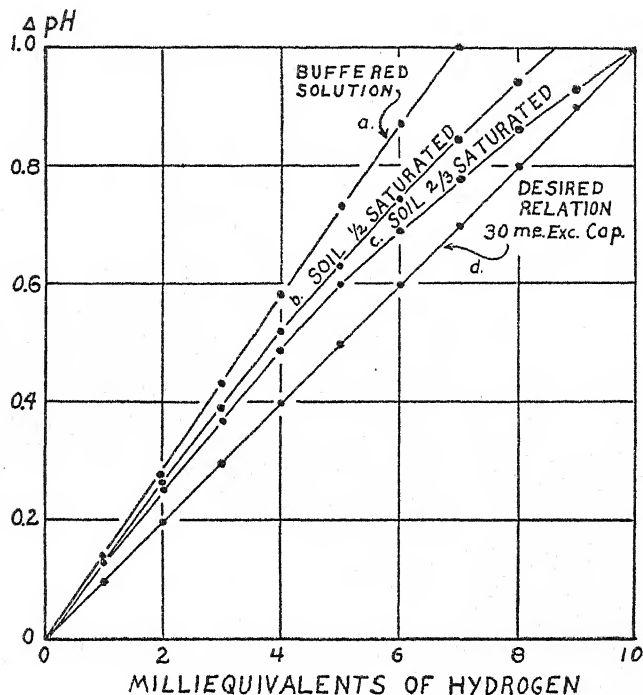


FIG. 3. DEPRESSION OF pH IN RELATION TO QUANTITY OF ACID ADDED TO A BUFFERED SOLUTION DESIGNED TO EXPRESS LIME REQUIREMENT OF SOIL IN TERMS OF COARSELY GROUND LIMESTONE

greatest for the soils of low exchange capacity, approaching +43 per cent as a limit for soils of negligible exchange capacity. It may be shown that the depression of the pH will not deviate more than 0.1 unit from the desired relation for soils up to 40 m.e. exchange capacity. The exchange capacity of few soils to be treated will exceed this value.

The solution possesses the necessary characteristics for the determination of lime requirement. For the heavy-textured soils, lime applied at the rate of 1,000 pounds per acre for each 0.1 unit depression of the pH corresponds to adding lime equivalent in amount to the exchangeable hydrogen that is present in the soil. For the light-textured soils, similar considerations will lead to the use of lime up to but not more than 43 per cent in excess of the exchangeable hydrogen

content of the soil. Overliming the light-textured soil is prevented, however, by the slowly available coarse material in the limestone. Results, some of which are reported in a later paragraph, are in excellent agreement with liming practices. Results reported by the author (6) and obtained by use of a solution of the above characteristics showed that the depression of the pH of a mixture of soil and solution measured the exchangeable hydrogen to within  $\pm 1$  m.e. per 100 gm. of soil, which is in agreement with the theoretical considerations advanced in conjunction with figure 3. The composition and use of this solution for determination of lime requirement are described below.

#### PROCEDURE FOR ROUTINE TESTING OF SOILS FOR LIME REQUIREMENT

A procedure adapted to routine testing of soils for lime requirement has been developed. It involves the use of a direct-reading pH instrument operated from the power line. This instrument is adjusted so that it reads exactly pH 7 when the electrodes are immersed in the buffered solution used for determining the lime requirement of the soil. This buffered solution, consisting of 8 gm. of *p*-nitrophenol, 40 gm. or 0.227 mole of calcium acetate and 0.62 gm. of magnesium oxide<sup>3</sup> per liter of solution, is adjusted initially to pH 7 with dilute HCl or MgO as required. Five grams of 10-mesh dry soil to be tested may be measured, rather than weighed, by using a small scoop of 1 inch depth and  $\frac{5}{8}$  inch diameter, cut from galvanized electrical conduit. A volume measure is preferable to a weight measure if the soil is not highly aggregated because the weight of an acre-plow-depth of soil is not constant. The accuracy of the volume measurement of the soil may be improved by using soil screened through a 40-mesh sieve. Waxed paper cups of 1 $\frac{1}{4}$ -ounce capacity, which may be discarded without washing, are excellent containers for the soil to be tested. Approximately 5 ml. of distilled water is added to the soil by a special rapid transfer pipette (5) and mixed by shaking preparatory to determining the pH with the glass electrode. Ten milliliters of the buffered solution, also measured with a rapid transfer pipette, is then mixed thoroughly with the soil and water. After standing 15 to 30 minutes, the mixture is stirred again before depression of the pH is read with the glass electrode. Each tenth pH unit depression corresponds to a requirement of 1,000 pounds of 10-mesh, mill-run limestone per acre-plow-depth of soil, provided the initial pH of the soil is below 6 to 6.5 indicating a need for lime. Soils that have been limed usually contain some hydrogen that depresses the pH of the buffer solution even though they are at pH 7, but the initially high pH reading eliminates these from further consideration.

The presence of significant quantities of exchangeable hydrogen in previously limed soils with pH levels in the vicinity of 6.5 has been observed. Liming of soils appears to coat the exterior of soil structural units, especially clays, so that

<sup>3</sup> During the course of this investigation, buffer solutions with the different cations Ca, Mg, Ba, Na, and K were studied. Solutions containing moderate concentrations of KCl in association with the buffering salts were also studied. All of these function satisfactorily with minor variations. The solution that is suggested was chosen because of the close resemblance of the cation composition to that of the soil.

the hydrogen on the interior of the particles becomes inactive with respect to the glass electrode. The pH of the soil determined with the glass electrode provides the best measure available of the character of the soil material that comes in contact with the plant roots. For that reason the initial pH of the soil-water mixture is used to decide whether the soil should be limed. The interpretation of the pH level at which lime should be applied varies among different investigators. This level has been established by most state experiment stations to fit their conditions of soils and the crop. A pH of 6.5 appears to represent a fairly ideal level, with values as low as 6.0 representing borderline cases in which reliming is to be recommended if this is convenient for the farmer.

The lime requirement based on depression of the pH of the buffered solution used according to the procedure described above is expressed in terms of 10-mesh, mill-run, high-calcium limestone. The Missouri Experiment Station (2) uses this type of lime as the basis for recommendations to farmers. When the quality

TABLE 1

*Relative quantities of different types of limestone to be used with reference to agricultural limestone based on percentage of the material passing through a 40-mesh sieve*

PERCENTAGE OF MATERIAL PASSING THROUGH A 40-MESH SIEVE	PERCENTAGE REQUIRED	
	Calcite	Dolomite
98	75	80
90	85	90
70*	100*	110
50	130	150
25	200	260

\* Agricultural ground limestone of high-calcium type used as standard of comparison.

of the limestone varies from this basic value, additional quantities may be added according to the table suggested by Coleman and Klemme (2) or by the chart suggested by Schollenberger and Salter (4). This chart has been used to prepare table 1, in which agricultural lime available at the end of one year has been used as a standard of comparison for other types of limestone based on the relative percentages passing through a 40-mesh sieve. Use of such a table permits adoption of a uniform procedure and expression of results for soil lime requirement, and is preferable to use of different concentrations of buffered solution that would be necessary for direct reading of lime requirement for specific types of liming materials. The above described procedure has been used extensively in Missouri, and the results are in close agreement with liming practices in the region.

#### RESULTS OF TESTS ON LIMED AND UNLIMED SOILS

A series of  $\frac{1}{20}$ -acre plots on the Missouri Experiment Station Field limed at different rates in the fall of 1940 and cropped to a 3-year rotation were sampled

in the fall of 1947 and studied with respect to lime requirement as measured by the procedure described above. The average results for ten samples from each plot, reported in table 2, show that 7 years after the initial treatment, the pH level of the soil and the growth of the recent seeding of alfalfa were satisfactory on the plot receiving 5,000 pounds of lime per acre, but not satisfactory where 2,500 pounds per acre had been used.

The sums of the limestone applied and the lime requirement readings total 6,400 pounds per acre on the more acid plots, while those on the less acid plots are greater, suggesting that the reaction between the lime and the soil is fairly complete on the acid soils but is still incomplete where the soil approaches neutrality. The indicated lime requirement of 6,400 pounds per acre for the original unlimed soil is 1,400 pounds greater than the 5,000 pounds which the results show has been adequate, but it approaches the quantity that would be required

TABLE 2  
*Lime requirement of plots receiving different amounts of limestone as determined by the procedure described for routine testing of soils*

LIMESTONE APPLIED	SOIL pH	LIME REQUIREMENT	SUM OF LIME REQUIREMENT AND LIME APPLIED	CONDITION OF ALFALFA
<i>lbs./A.</i>		<i>lbs./A.</i>	<i>lbs./A.</i>	
1500	5.3	4900	6400	None
2500	5.7	3900	6400	None
5000	6.5	1800	6800	Good
7500	7.2	500	8000	Good

to bring the soil to pH 7. The limestone used was of the 10-mesh, mill-run type with a high percentage of the finer fractions.

York and Rogers (7) have reported decreased yields of *Sericea* following use of 3 tons of lime per acre on Hartsells fine sandy loam, but satisfactory yields where 1 ton of lime was used. The original pH of this soil was reported by them as 5.1 and the exchange capacity as 3.1 m.e. per 100 gm. of soil. A sample of the same soil supplied by York and Rogers depressed the pH of the buffered solution 0.2 pH unit, indicating a lime requirement of only 2,000 pounds per acre, irrespective of the low pH value of the soil, checking the results they obtained by growing plants.

#### SUMMARY

The theory and use of a buffered solution for determining the lime requirement of soil have been presented. A procedure for routine testing of soils is described. The pH of the soil is used as an indication of whether or not the soil should be limed. If the initial pH of the soil is below the level considered desirable for growth of legumes, the amount of 10-mesh, mill-run agricultural limestone to be applied is determined by measuring the depression of the pH of a buffered solution in contact with the soil. The results obtained with the method indicate that

it is quick, reliable, and adaptable to use on soils of different exchange capacities with the assurance that adequate quantities of limestone will be indicated without danger of overliming.

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# EFFECT OF CALCIUM AND BORON NUTRITION OF THE TOMATO ON THE RELATION BETWEEN THESE ELEMENTS IN THE TISSUES<sup>1</sup>

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That the functions of boron and calcium are intimately associated in the general metabolic activities of the plant has been recognized for the last 20 years. Many of the early investigations dealt with descriptions of boron-deficiency and -toxicity symptoms resulting from different amounts of boron in the substrate (3, 8, 12). They reported a general association between the severity of the symptoms and the method of liming and fertilizing the soil. In recent years there has been a trend toward a quantitative type of investigation to obtain a more complete understanding of the chemical and physiological relationship which exists between calcium and boron (4, 6, 7, 10, 11). Practical value as well as scientific interest is involved in the subject. The purpose of this investigation was to study quantitatively the effect of variations of boron and calcium in the substrate on the accumulation and distribution of these elements in various tissue fractions of tomato plants.

## PLAN OF EXPERIMENT

### *Cultural methods*

In June 1945, Marglobe tomato seeds were germinated in sand. When the cotyledons were free from the seed coat and the first true leaves still in the bud stage, the seedlings were transplanted into acid- and alkali-washed white quartz sand in glazed pots. Three plants were put in each pot. Nutrient solution was supplied by the continuous flow method. For 10 days after being transplanted, all cultures were supplied with a complete nutrient solution containing 0.25 p.p.m. boron and 180 p.p.m. calcium. Calcium-boron treatments were begun at the end of this period and maintained for 26 days. Five calcium levels were employed—5, 50, 100, 250, and 500 p.p.m.—and at each calcium level four boron concentrations were used—0.001, 0.10, 0.25, and 5.0 p.p.m.—, making a total of 20 treatments. The composition of the culture solutions is presented in table 1.

At the end of the experimental period of 26 days, the plants were harvested. The plants from each treatment were divided into four fractions: upper leaves, upper stems and petioles, lower leaves, and lower stems and petioles. Green and dry weights of each fraction were obtained. Part of each fraction was quickly frozen at the time of harvest for the determination of the soluble com-

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of plant physiology.

<sup>2</sup> Grateful acknowledgment is hereby accorded W. Rei Robbins for his valuable assistance in preparing this paper for publication.

ponents of the calcium and boron in the plants. The remaining tissue was dried in preparation for determination of total calcium and boron. Plants grown under conditions of low calcium and low boron did not provide enough tissue for fractionation, and therefore the entire plant was taken as a single sample for analysis.

#### *Analytical methods*

Dry yields of each fraction of tissue were obtained by drying samples for 48 hours at 70°C. The dried tissue was ground in a semimicro Wiley mill to pass a 40-mesh screen. A 2-gm. sample was ignited in a porcelain crucible in a muffle furnace at 600°C. The residue was taken up in 20 ml. of (1 + 4) HCl and made up to volume with distilled water in a 100-ml. volumetric flask. Where insufficient tissue was available, a 1-gm. sample was ignited and the residue was made up to 50 ml.

TABLE 1  
*Composition of culture solutions at five calcium levels employed with each of the four different boron concentrations of 0.001, 0.1, 0.5, and 5.0 p.p.m.\**

Ca LEVELS	MOLAR CONCENTRATION OF MAJOR SALTS					
	KH <sub>2</sub> PO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	MgSO <sub>4</sub>	CaCl <sub>2</sub>	CaSO <sub>4</sub>
<i>p.p.m.</i>						
5	0.00113	0.00226	0.0085	0.00113	0.000125	.....
50	0.00113	0.00226	0.0085	0.00113	0.00125	.....
100	0.00113	0.00226	0.0085	0.00113	0.00250	.....
250	0.00113	0.00226	0.0085	0.00113	0.00625	.....
500	0.00113	0.00226	0.0085	0.00113	0.00625	0.00625
Preliminary standard solution.....	.00225	.00056	....	.00225	.....	Ca(NO <sub>3</sub> ) <sub>2</sub> .0045

\* Each solution also contained 1 p.p.m. Fe, 0.5 p.p.m. Zn, and 0.25 p.p.m. Mn.

It is assumed that the metabolically active portions of boron and of calcium in the plant tissues are those present in soluble form. These soluble fractions were extracted from the frozen samples under pressure. Portions of calcium and of boron remaining in the press cake are considered to be insoluble or inactive.

During extraction the frozen tissue was wrapped in a small square of muslin, placed in a Carver pressure chamber, covered with 40 ml. of distilled water, and subjected to a pressure of 2,500 pounds per square inch for 1 minute. The press cake was washed twice more with 40-ml. portions of distilled water and after each washing was subjected to the same pressure. After the last washing, pressure was maintained for 2 minutes. The washings were passed through a Whatman No. 5 filter paper. The press cake and filter paper were dried in the oven at 70°C. for 48 hours, and were then ignited in a muffle furnace at 600°C. The residue was taken up in 20 ml. of (1 + 4) HCl and made up to volume with

distilled water in a 100-ml. volumetric flask. Aliquots of this solution were taken for determination of the boron and calcium representing the insoluble portions in the tissue.

The soluble calcium and boron content of each tissue fraction was determined by subtracting the amount of each element obtained by analysis of the entire residue of an extracted sample from the calcium and boron content of the corresponding unextracted tissue sample.

Calcium determinations were made by the volumetric methods of the A.O.A.C. (1). The Berger and Truog colorimetric method using quinalizarin was used for the boron analyses (2). Instead of 98 per cent sulfuric acid, 96.9 per cent was used.

#### RESPONSE OF PLANTS TO TREATMENT

At the end of the experimental period, all the plants grown at the lowest boron level of 0.001 p.p.m. exhibited typical boron-deficiency symptoms. Those plants which had received a high calcium concentration (500 p.p.m.) in combination with the low boron level were most severely injured, whereas at the lowest calcium level in combination with this same low boron concentration the plants were only slightly injured. In the boron-deficient plants the terminal growing point died, and the stems and petioles became extremely brittle. This brittleness accompanied by the sloughing off of cells has been attributed to the failure of the middle lamella of calcium pectate to develop (9). The root systems of these boron-deficient plants were small and brown, indicating early maturity. Boron-toxicity symptoms consisting of brown areas on the margins of the lower leaves appeared to some extent on all cultures receiving 5.0 p.p.m. boron. These symptoms increased in severity with decreasing concentrations of calcium in the substrate. Plants grown in a nutrient solution containing 0.10 and 0.25 p.p.m. boron were entirely normal in appearance except at the 5 p.p.m. calcium level, where calcium-deficiency symptoms characterized by the curling of the young leaves were observed.

As shown in table 2, the average green weight per plant at each boron level increased as the calcium in the substrate was increased. At the lowest boron level the total green weights were lower than those at the higher boron levels.

#### RESULTS OF CHEMICAL ANALYSES

The results of quantitative tests for total and soluble boron and calcium contents of the four tissue fractions of plants grown under the 20 different calcium-boron treatments are given in tables 3, 4, 5, and 6.

##### *Boron content*

Certain trends in the distribution of boron in the plant were observed in this experiment. The highest amount of total and soluble boron per gram of dry tissue occurred in the lower leaves. The upper leaves contained much less boron than did the lower leaves. The stems accumulated less boron than did the leaves. Lower stems and upper stems had approximately the same total

boron content, but the soluble boron content of the lower stems exceeded that of the upper stems in most cases. After studying 50 plant species, Eaton (5) reported that, with stone fruits as known exceptions, boron tends to accumulate in highest concentrations in the leaves of plants and to be present in relatively low concentrations in roots, wood, fruit, and other storage and meristematic tissues.

In general, the amount of boron found in each tissue fraction of the tomato plant varied directly with the concentration of boron in the nutrient solution.

TABLE 2  
*Green and per cent dry weights of tomato plant tissue*

NUTRIENT TREATMENT		UPPER LEAVES		UPPER STEMS		LOWER LEAVES		LOWER STEMS		TOTAL
Ca	B	Green weight	Per cent age of dry weight	Green weight	Per cent age of dry weight	Green weight	Per cent age of dry weight	Green weight	Per cent age of dry weight	Green weight
<i>p.p.m.</i>	<i>p.p.m.</i>	<i>gm.</i>		<i>gm.</i>		<i>gm.</i>		<i>gm.</i>		<i>gm.</i>
5	0.001	....	....	....	....	....	....	....	....	38.8
50	0.001	....	....	....	....	....	....	....	....	130.5
100	0.001	38.0	12.6	51.5	6.6	19.5	14.4	38.0	6.6	147.0
250	0.001	31.5	14.6	38.5	4.4	32.0	11.3	69.7	7.2	171.7
500	0.001	37.5	14.8	40.8	6.4	53.6	12.3	79.7	8.2	211.6
5	0.10	....	....	....	....	....	....	....	....	76.9
50	0.10	64.5	12.6	81.1	5.4	47.0	9.15	82.7	6.9	275.3
100	0.10	66.2	14.4	73.5	6.8	50.5	11.9	94.5	8.0	284.7
250	0.10	77.1	16.3	64.8	7.6	77.9	12.2	115.9	7.9	315.7
500	0.10	62.8	16.4	84.3	7.0	76.8	12.4	119.0	8.9	342.9
5	0.25	....	....	....	....	....	....	....	....	73.4
50	0.25	79.8	11.5	89.8	5.8	35.6	8.99	71.0	7.3	276.2
100	0.25	59.8	19.7	68.6	7.0	72.5	11.3	111.8	8.5	312.7
250	0.25	60.9	14.1	46.8	6.8	60.9	10.8	109.6	8.2	278.2
500	0.25	50.7	16.2	58.4	6.8	79.0	12.8	116.6	9.0	304.7
5	5.0	....	....	....	....	....	....	....	....	80.3
50	5.0	54.0	14.3	61.0	5.2	27.6	11.6	72.2	6.9	214.8
100	5.0	41.5	14.2	46.5	4.5	59.6	12.1	95.3	7.0	242.9
250	5.0	48.0	14.7	47.3	4.9	71.0	11.3	108.3	6.6	274.6
500	5.0	73.7	15.1	76.4	6.9	67.7	12.0	101.2	8.7	319.0

The leaves were most responsive to changes in concentrations of boron in the substrate. At a given calcium level, as the boron concentration was increased in the substrate, the following trends were observed:

The total and soluble boron content of the upper leaves increased markedly.

The total and soluble boron content of the lower leaves increased except in three cases.

The total and soluble boron content of the upper stems tended to increase except at the 5.0 p.p.m. boron level in combination with the two highest calcium levels.

The total and soluble boron content of the lower stems generally increased except at the 5.0 p.p.m. boron level in combination with 500 p.p.m. calcium.



TABLE 3

*Total and soluble boron and calcium contents of upper leaves of tomato plant*  
In milligrams per gram of dry tissue

NUTRIENT TREATMENT		TOTAL B	SOLUBLE B	TOTAL Ca	SOLUBLE Ca
Ca	B				
<i>p.p.m.</i>	<i>p.p.m.</i>				
50	0.001	.....	.....	.....	.....
100	0.001	.0300	.0039	30.0	12.1
250	0.001	.0200	.0034	21.3	6.9
500	0.001	.0200	.0000	23.5	5.6
50	0.10	.0500	.0267	14.2	0.5
100	0.10	.0500	.0250	20.8	6.7
250	0.10	.0650	.0422	22.9	6.0
500	0.10	.0400	.0250	22.6	4.4
50	0.25	.0750	.0359	15.1	0.3
100	0.25	.0500	.0327	14.6	7.1
250	0.25	.0750	.0522	19.6	3.0
500	0.25	.0500	.0335	25.2	6.3
50	5.0	.5000	.4025	15.0	7.5
100	5.0	.4500	.3210	15.8	4.0
250	5.0	.3000	.2167	18.1	2.7
500	5.0	.4000	.2814	28.5	6.9

TABLE 4

*Total and soluble boron and calcium contents of lower leaves of tomato plant*  
In milligrams per gram of dry tissue

NUTRIENT TREATMENT		TOTAL B	SOLUBLE B	TOTAL Ca	SOLUBLE Ca
Ca	B				
<i>p.p.m.</i>	<i>p.p.m.</i>				
50	0.001	.....	.....	.....	.....
100	0.001	.0100	.0023	23.8	6.9
250	0.001	.0270	.0113	50.6	22.7
500	0.001	.0200	.0024	46.3	15.1
50	0.10	.0750	.0417	32.4	14.6
100	0.10	.1250	.0766	36.5	10.4
250	0.10	.0750	.0568	44.5	21.9
500	0.10	.0900	.0743	51.8	26.0
50	0.25	.1000	.0464	35.4	16.7
100	0.25	.0750	.0397	34.5	15.2
250	0.25	.1000	.0706	49.3	28.4
500	0.25	.1000	.0673	46.6	15.8
50	5.0	.7500	.4167	26.3	9.1
100	5.0	.9000	.7056	34.7	14.8
250	5.0	.7500	.6037	40.7	10.6
500	5.0	.4500	.2682	51.4	20.4

At a given boron level the influence exerted by changes in the concentration of calcium in the substrate on the accumulation of boron in the plant depended on the particular tissue and the boron level involved. In the upper leaves, with boron constant at 0.001 p.p.m., as the calcium in the substrate was increased, the total and soluble boron tended to decrease. This reduction in boron content, if confirmed in future investigations, suggests an explanation for the qualitative observations made on these plants at the time of harvest, when it was noted that boron-deficiency symptoms occurring on the upper leaves of the plant became more severe as the calcium concentration in the substrate was increased.

TABLE 5  
*Total and soluble boron and calcium contents of upper stems of tomato plants*  
In milligrams per gram of dry tissue

NUTRIENT TREATMENT		TOTAL B	SOLUBLE B	TOTAL Ca	SOLUBLE Ca
Ca	B				
<i>p.p.m.</i>	<i>p.p.m.</i>				
50	0.001	....	....	....	....
100	0.001	.0200	.0024	20.0	4.1
250	0.001	.0200	.0019	31.2	7.5
500	0.001	.0300	.0086	19.2	4.8
50	0.10	.0400	.0139	7.4	0.7
100	0.10	.0400	.0054	13.2	8.0
250	0.10	.0300	.0069	15.0	2.4
500	0.10	.0300	.0107	19.5	6.7
50	0.25	.0500	.0231	7.3	0.4
100	0.25	.0400	.0104	9.9	0.1
250	0.25	.0500	.0233	16.9	6.9
500	0.25	.0400	.0200	16.2	1.0
50	5.0	.0750	.0221	8.1	1.8
100	5.0	.0750	.0209	9.8	0.6
250	5.0	.0500	.0091	17.8	2.5
500	5.0	.0300	.0050	19.8	0.1

The plants which exhibited the most severe injury from boron deficiency were those at 500 p.p.m. calcium and 0.001 p.p.m. boron, giving evidence of *no* soluble boron in the upper leaves. Under conditions of very low boron and increasing levels of calcium, the other tissue fractions showed no definite trend with respect to boron content. With boron constant in the substrate at 0.10 and at 0.25 p.p.m., as the calcium level in the substrate was increased, there was no definite relation between the quantity of boron accumulated in any tissue and the amount of calcium in the substrate. With boron constant at 5.0 p.p.m., as the calcium in the substrate was increased, the amount of total and soluble boron in the upper and lower stems decreased markedly and that in the upper and lower leaves showed a tendency to decrease. At this boron level quantitative data supported

qualitative observations, that is, that boron-toxicity symptoms at the highest boron level were most severe on plants grown in a substrate containing low calcium and least severe on plants grown with the highest calcium level. In plants grown at the 5.0 p.p.m. boron level in combination with 50, 100, or 250 p.p.m. calcium, the lower leaves were found to contain a greater amount of soluble boron than the lower leaves of plants grown at 5.0 p.p.m. boron and 500 p.p.m. calcium. This indicates that with low calcium a larger amount of boron in the plant accumulates as soluble boron and becomes toxic, and that with high tissue con-

TABLE 6

*Total and soluble boron and calcium contents of lower stems of tomato plants*  
In milligrams per gram of dry tissue

NUTRIENT TREATMENT		TOTAL B	SOLUBLE B	TOTAL Ca	SOLUBLE Ca
Ca	B				
<i>p.p.m.</i>	<i>p.p.m.</i>				
50	0.001	.....	.....	.....	.....
100	0.001	.0300	.0135	15.8	1.2
250	0.001	.0300	.0140	22.7	2.3
500	0.001	.0200	.0034	21.7	0.6
50	0.10	.0400	.0159	12.1	0.1
100	0.10	.0300	.0250	18.5	1.3
250	0.10	.0400	.0216	23.9	0.3
500	0.10	.0300	.0275	29.3	0.4
50	0.25	.0500	.0278	12.7	1.3
100	0.25	.0400	.0155	19.3	2.7
250	0.25	.0400	.0237	22.7	0.8
500	0.25	.0500	.0376	24.4	3.8
50	5.0	.0750	.0442	12.0	0.8
100	5.0	.0500	.0188	18.6	0.1
250	5.0	.0500	.0263	26.9	1.8
500	5.0	.0300	.0012	26.7	2.0

tents of calcium excess soluble boron is rendered insoluble and harmless. Two cases of the inhibiting effect of high calcium concentration on the accumulation of boron in the plant have been cited here. High calcium served to accentuate the severity of the boron-deficiency symptoms at the lowest boron level, and to allay the boron-toxicity symptoms at the highest boron level. Such data may, in part, explain similar responses long observed as a result of applying varied amounts of lime to the soil.

#### *Calcium content*

Distribution of calcium in the leaves followed the same pattern as that of boron. At a given level of calcium in the substrate, lower leaves had a higher total and soluble calcium content than upper leaves. This indicates that the

calcium was not freely translocated from the older to the younger tissues. The lower stems contained more total calcium than the upper stems except in two treatments at the lowest boron level, but the upper stems had a greater amount of soluble calcium in most cases. The quantity of soluble calcium found in the tissues did not appear to be related to the total calcium in the plant, to the calcium present in the substrate, or to the total or soluble boron in the tissues. At a given boron level, increments in the concentration of calcium in the substrate generally resulted in an increased accumulation of total calcium in the tissues. One important exception to this relation occurred in the upper leaves of plants

TABLE 7  
*Ratio of total calcium to total boron in tomato plant tissues*

TREATMENT		UPPER LEAVES	LOWER LEAVES	UPPER STEMS	LOWER STEMS
Ca	B				
<i>p.p.m.</i>	<i>p.p.m.</i>				
50	0.001	.....	.....	.....	.....
100	0.001	1000	2380	1000	527
250	0.001	1065	1874	1560	757
500	0.001	1175	2315	640	1085
50	0.10	284	432	185	303
100	0.10	416	292	330	617
250	0.10	352	593	500	598
500	0.10	565	574	650	977
50	0.25	201	354	146	254
100	0.25	292	460	248	483
250	0.25	261	493	338	568
500	0.25	504	466	405	488
50	5.0	30	35	108	160
100	5.0	35	39	131	372
250	5.0	60	54	356	538
500	5.0	70	114	660	890

grown with a nutrient solution containing 500 p.p.m. calcium and 0.001 p.p.m. boron.

An increase in the concentration of boron in the substrate at any given calcium level was not significantly related to changes in the calcium content of the tissues.

#### *Calcium-boron ratios*

To determine a means of relating plant response to variations in the nutrient levels of calcium and boron, the ratios of total calcium to total boron in the various tissue fractions were calculated (table 7). The leaf tissues of boron-deficient plants had extremely high calcium-boron ratios, ranging from 1,000 to 2,380. The leaf tissues of boron-toxic plants had a low ratio of total calcium to total boron, ranging from 30 to 114. Leaf tissues of plants grown with the in-

intermediate boron levels of 0.10 and 0.25 p.p.m. had intermediate calcium-boron ratios, ranging from 201 to 593. As a general rule, the ratio of total calcium to total boron was considerably higher in the lower leaves than in the upper leaves. Likewise, the calcium-boron ratios calculated for the lower stems were higher than those of the upper stems except at the lowest boron level. This may be attributed largely to the relatively high calcium contents of the older tissues of the plant. Throughout the experiment the values of the calcium-boron ratios varied over a wider range in the leaves than in the stems. As the calcium in the substrate was increased at a given boron level, the ratio of calcium to boron increased in most cases. As the boron in the substrate was increased at a given calcium level, the calcium-boron ratio in the plant decreased.

### *Discussion*

A consideration of the ratio of total calcium to total boron in plant tissue emphasizes the significance of the relationship between the two elements. In every case the leaves of plants supplied with a complete nutrient solution containing sufficient boron and calcium for normal growth had intermediate numerical ratios of calcium to boron ranging from 201 to 593. Any deviation from this intermediate range of calcium-boron ratios in the leaves was related to a departure from the normal metabolism of the plant. With the normal calcium-boron ratio established, it may serve as a criterion for judging the condition of plants grown in substrates varying in calcium and boron.

When the plants were grown at the lowest boron level, 0.001 p.p.m., regardless of the amount of calcium supplied at that time, the ratio of calcium to boron in the leaf tissues was extremely high, in one case amounting to 2,380. When the plants were grown at the highest boron level, the calcium-boron ratios in the leaves were extremely low, ranging from 30 to 114. The calcium-boron ratios of the stem tissues of these plants compared much more favorably with those of normal plants. As the calcium was increased in the substrate at the highest boron level, the calcium-boron ratio for each tissue increased. Thus a combination of the highest level of calcium and 5.0 p.p.m. boron in the substrate produced plants with calcium-boron ratios approximating those of normal plants.

With a knowledge of the normal calcium-boron ratios for a given plant species, the calcium-boron ratios of the same species grown under various nutrient treatment can be interpreted. In fact, their course of metabolism may be predicted from the nature of these ratios. The exact numerical ratios established here for normal and abnormal tomato plants may not be found in other plant species, but undoubtedly the same trends will exist.

From these data it is reasonable to suggest that the total calcium-boron ratio of the plant may serve not only to explain the condition of the plant but also to indicate, in turn, the status, with respect to availability of these element, of the soil in which the plant was grown. This method has the advantage over a chemical analysis of the soil for total calcium and boron in that it takes into consideration a significant relationship between the elements in the tissue and is, therefore, a measure of the calcium and boron actually available to the plant.



## SUMMARY

A quantitative study of the response of tomato plants to varied calcium-boron concentrations in the nutrient solution brought out the following major points:

In a normal plant the distribution of boron followed a definite pattern. Lower leaves contained a much higher amount of total and soluble boron than upper leaves. Lower and upper stems had approximately the same boron content but much less than that found in leaf tissue.

Increments in the boron concentration in the substrate caused a marked increase in boron content of the leaves but only a slight increase in boron content of the stems.

The effect produced on the boron content in the tissue by an increase of calcium in the substrate varied in the following manner:

Increments in the calcium concentration in the substrate at a very low boron level (0.001 p.p.m.) caused a decrease in the boron content of upper leaves but no definite effect in the other tissue fractions.

Increments in the calcium concentration in the substrate at intermediate boron levels (0.10 and 0.25 p.p.m.) produced no definite influence on the amount of boron accumulated in any tissue fraction.

Increments in the calcium concentration in the substrate at the highest boron level (5 p.p.m.) generally caused a decrease in the boron content of each tissue fraction.

Plants with external symptoms of boron deficiency were found on analysis to contain little total and soluble boron in any of the tissues.

Symptoms of boron deficiency on tomato plants were accentuated by a high calcium concentration in the substrate. Chemical analysis corroborated visual observations showing low boron in the tissues, especially the upper leaves.

Plants with external symptoms of boron toxicity showed on analysis very high content of total and soluble boron in all the tissues.

Symptoms of boron toxicity on plants receiving low calcium in the substrate were more severe than on those receiving high calcium. Chemical analysis revealed a high boron content especially in the lower leaves, again substantiating visual observations.

Total calcium in the tissues was determined by the calcium concentration of the substrate and apparently was independent of boron. The soluble calcium in the plant tissue appeared not to be a function of total calcium in the tissue, total calcium in the substrate or of boron.

The ratio of total calcium to total boron in the tissues, especially the leaves, reflected the treatments under which the plants had been grown.

The calcium-boron ratio in leaves of normal tomato plants ranged from 201 to 593; in leaves of boron-toxic plants, from 30 to 114; and in leaves of boron-deficient plants, from 1,000 to 2,380.

At any given boron level, the calcium-boron ratio in the tissue increased markedly with an increase in calcium concentration in the substrate.

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## BOOKS

*An Approach Toward a Rational Classification of Climate.* By C. W. THORNTWAITE. The Geographical Review, vol. 38, pp. 55-94, American Geographical Society, New York, 1948.

The approach in this presentation is that of examining the climate of the United States in relation to crop needs. Classification of the climate is reduced to a simple expression of four symbols. These are illustrated on four large colored maps, labeled moisture regions of the United States, seasonal variation of effective moisture, average annual thermal efficiency, and summer concentration of thermal efficiency.

*Chemicals, Humus, and the Soil.* By DONALD P. HOPKINS. Chemical Publishing Co., Inc., Brooklyn, 1948. Pp. 358. Price \$8.50.

This is an American edition of the book of the same title that was reviewed in the May, 1947, issue of SOIL SCIENCE. The text is essentially unchanged. The points of view and the illustrative examples are British. The author undertakes a careful analysis of the case for and against fertilizers. The first half of the book is an orthodox presentation of the principles of fertilizer practice and the importance of fertilizers as agents for improving the productivity of soils. The remainder of the book deals with the modern counter-argument, with such chapter titles as "Humus and Health," "Plant Disease," and "Food Values and Chemicals," concerning which so much is being written by the antifertilizer group. The author succeeds admirably in his presentation of the pros and cons. The appendix gives specific suggestions on meeting the fertilizer needs of various crops and presents a bibliography of 21 technical, general, and humus-school books, with short reviews of their nature and contents. The book merits a wide reading, especially by those who may have been unduly disturbed by the teachings of propagandists for the "biodynamic" system of farming.

*The Cookability of Yellow Peas.* By SANTE MATTSON. Acta Agriculturae Suecana, pp. 185-231, The Royal Swedish Academy of Agriculture, Stockholm, 1946.

The cookability of peas was found to depend upon the nature and valence of the cations in combination with the pea acidoids. Peas saturated with monovalent cations, including H ions, were soft-cooking, whereas those saturated with Ca and Mg were uncookable. The cookability was improved by addition of precipitants, including oxalate, phosphate, and carbonate ions.

*Dynamique du Sol.* Fourth edition. By ALBERT DEMOLON. Dunod, Paris, 1948. Pp. 414, figs. 119.

This book consists of a revised series of lectures that were given at the Conservatoire des Arts et Métiers in Paris in 1930. The general character of the presentation is the same as in earlier editions, but the experimental data and the

principles established therefrom have been brought up to date. The several chapters deal with general ideas about the parent rocks, genetic classification of soils, soils of France and the Colonies, colloidal minerals in soils, colloidal humus, mechanical analyses of soils, soil structure, soil-water relationships, soil climate, the adsorbent complex, the soil solution, soil reaction, soils in relation to plant needs, soil population, organic matter relationships in soils, nitrogen and sulfur relationships, and some ideas on soil fertility. A list of references is included at the end of each chapter, and methods of soil analyses are given in the appendix. The book is especially useful for graduate students who desire to improve their capacity to read French and at the same time to obtain some new concepts about soils.

*Electrochemical Analysis with Graded Cathode Potential Control.* By HARVEY DIEHL. The G. Frederick Smith Chemical Co., Columbus, Ohio, 1948. Pp. 56, figs. 9.

The theory and the practice of effecting the separation of certain metals by electro-deposition are presented in this booklet, which describes and illustrates the necessary apparatus and reviews the literature as related to silver, copper, bismuth, antimony, lead, tin, nickel, and cadmium. A full-page photograph of Henry S. J. Sand, the inventor of the graded cathode potential method of analysis, is shown.

*Eruptive Rocks.* Third edition. By S. JAMES SHAND. John Wiley & Sons, Inc., New York, 1947. Pp. 488, plates 4, figs. 51.

This book deals with the genesis, composition, and classification of eruptive rocks and their relation to ore deposits. It also contains a very interesting chapter on meteorites. The book was written with the purpose of "cleaning up the jungle of rock names," making petrology intelligible to the chemist, and bringing theory and practice together so that geology becomes something more than an academic study. For the third edition, a greater effort was made than in the earlier editions to develop the connection between eruptive rocks and ore deposits. The four chapters that show the author's system of classification of rocks now form Part II of the book. Rocks are classified into four groups: the oversaturated rocks, such as granite; the saturated, such as syenite and diorite; the undersaturated non-feldspathoidal, such as peridotite; and the undersaturated feldspathoidal, such as leucite-phonolite. A well-developed list of references is appended to each chapter. The book is an excellent reference work for advanced students of the subject.

*Forecasts of the Population of the United States 1945-1975.* By P. K. WHELPTON. U. S. Department of Commerce Bureau of the Census, 1948. Pp. 113, figs. 8. Can be obtained from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. Price \$0.45.

A very important publication dealing with mortality trends, fertility trends,



immigration and future population growth, indicated population changes, implications of the expected population trends, and supporting figures and tables. All those who have to do with the problems of food production will find this a very interesting and thought-provoking presentation.

*Growth of Plants.* By WILLIAM CROCKER. Reinhold Publishing Corporation, New York, 1948. Pp. 459, figs. 171. Price \$10.

This is a unique book in that it deals with a series of special studies of plants and plant processes under conditions of rigid control. The chapter titles include life span of plants, dormancy in seeds, physiological effects of ethylene and other unsaturated carbon-containing gases, effects of certain lethal gases (illuminating gas, mercury vapor, sulfur dioxide, chlorine, hydrogen cyanide, and hydrogen sulfide) upon plants and animals, plant hormones, dormancy in buds (and metabolic changes induced by ethylene chlorhydrin), plant cell membranes (with special reference to cotton), plants grown under controlled environmental conditions, insecticides, and fungicides. The introduction tells the story of the founder, William Boyce Thompson. Among the early problems studied were virus diseases of plants, duck food, and aquatic plants. Among the miscellaneous studies were those on discoloration of potato chips, autumn changes in the leaves of deciduous plants, the isoelectric point in protoplasm, growth substances and vitamin B<sub>1</sub> for seed treatment, flower color of hydrangeas, and those on *Lilium*, *Gladiolus*, *Dahlia*, *Arbutus*, and *lycopodium*. Specific references to the work of some 350 scientists are appended to the several chapters. Most frequent reference is made to the work of Lela Barton, William Crocker, F. E. Denny, J. D. Guthrie, A. E. Hitchcock, S. E. McCallen, N. C. Thornton, F. Wilcoxon, and P. W. Zimmerman. The illustrations are excellent. All workers in plant science will find great inspiration and much factual information in this highly important contribution to the literature in this field.

*The Hybrid Corn Makers.* By A. RICHARD CRABB. Rutgers University Press, New Brunswick, N. J., 1947. Pp. 331. Price \$3.

This history of the development of hybrid corn and the doings of the men who made it possible begins with the story of the corn which the Indians grew, takes the reader through the period of the development of corn hybrids, and ends with a look into the future of this remarkable plant. Eugene Davenport and Cyril G. Hopkins are given credit for arousing interest in the possibilities of improving the corn plant and for getting the first important research program with it under way. The project takes on new interest with the pioneering breeding work of Edward M. East and George H. Shull. As the subject is developed, such names as H. H. Love, E. G. Montgomery, T. A. Kisselbach, H. K. Hayes, D. F. Jones, F. D. Richey, George N. Hoffer, J. R. Holbert, Gene Funk, Henry A. Wallace, Lester Pfister, and many others pass in review. The book presents a factual and fascinating report of one of the most remarkable developments in the agricultural history of the United States.

*Plant and Soil.* Volume 1, Number 1. Issued under the auspices of the Netherlands Society of Agricultural Science, Martinus Nijhoff N.V., 9 Lange Voorhout, The Hague, 1948. Pp. 119, figs. 31. Price 20 guilders per volume.

This is the first issue of an "international journal of plant nutrition, plant chemistry, soil microbiology, and soil-borne plant diseases." Four issues will be published annually, each volume containing about 400 pages. Manuscripts must be written either in English, French, or German. Included among the executive editors is D. I. Arnon of California and among the consulting editors are Wm. G. Albrecht of Missouri, D. R. Hoagland of California, and S. A. Waksman of New Jersey. The first issue contains six articles: Determination of biotin in beet molasses with *Neurospora crassa* Shear and Dodge as a test organism; Utilization des engrais phosphatés par les plantes, après leur absorption dans le sol; Neuere Beobachtungen über die Ursachen der Dörrfleckenkrankheit beim Hafer; The influence of microorganisms on the phosphate intake of the plant; Reaction changes in the life-medium of plants caused by differential intake of ions; and Importance of molybdenum in the nitrogen metabolism of microorganisms and higher plants. The journal has an attractive cover, the paper is of high quality, and the printing and illustrations are excellent. It seems probable that it will serve a very useful purpose and that experiment station workers in soil and plant sciences will find it of much interest and value.

*Practical Field Crop Production for the Northeast.* Edited by VAN WIE INGHAM. Rutgers University Press, New Brunswick, N. J., 1947. Pp. 437, figs. 145. Price \$4.

The authors of this book are Gilbert H. Ahlgren, Robert A. Snell, John C. Anderson, and Milton A. Sprague, all members of the farm crops staff of the New Jersey Agricultural Experiment Station. The book is an elementary presentation of the subject of farm crops with special reference to the region, which includes Ohio on the west and West Virginia and Maryland on the south. The emphasis is on hay, pasture, and silage crops, but consideration is also given to corn, small grains, potatoes, soybeans, and tobacco. Chapters on weeds and weed control are also included. Suggested reading and visual aids are appended to each chapter. The appendix includes crop varieties recommended for the region, weights and measures used in agriculture, and a glossary of technical terms. The book is well illustrated, and the material is attractively presented. The level of presentation is that of the agricultural high school or of a college freshman course in farm crops.

*Preparation and Measurement of Isotopic Isomers.* Edited by D. WRIGHT WILSON. J. W. Edwards, Inc., Ann Arbor, Michigan, 1947. Pp. 108. Litho-printed, paper-bound. Price \$1.80.

This is a symposium prepared for the Isotope Research Group to acquaint biologists and chemists with methods of preparation and analysis of isotopes, with special reference to carbon and hydrogen. The papers deal with separation of stable isotopes, mass spectrometry, preparation of gas samples, preparation of

carbon dioxide samples, the falling drop method for determination of deuterium, determination of deuterium, production of radioisotopes of hydrogen, carbon, and sulfur, and detection and measurement of radioactive tracers. The authors are H. G. Thode, Alfred O. Nier, David Rittenberg, S. Weinhouse, Mildred Colin, Chris Anfinsen, Martin D. Kamen, and Allen R. Reid. Most of the papers contain several figures and a number of references.

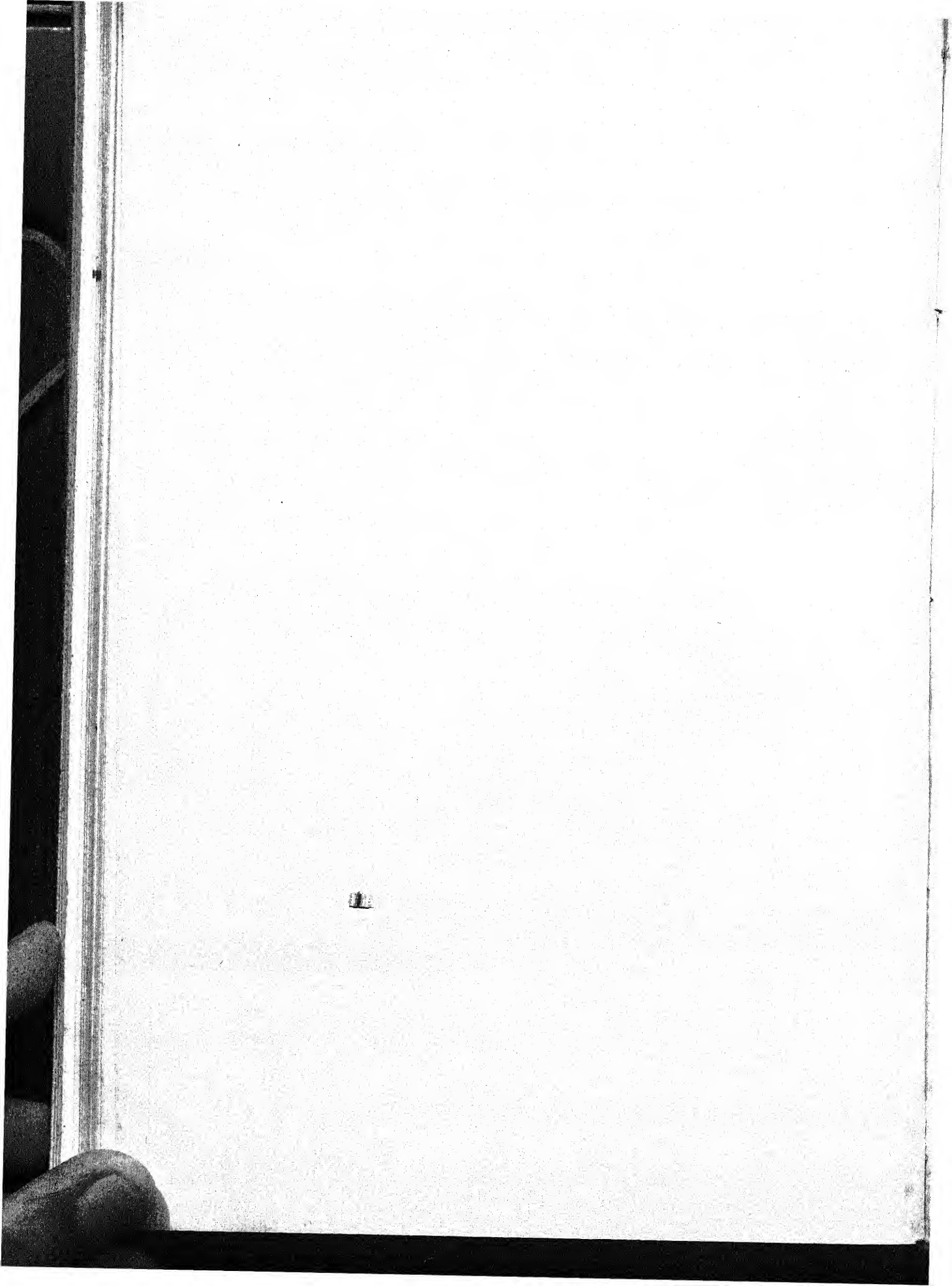
*Report of the Waste Conversion Committee of the State of Rhode Island and Providence Plantations.* THEODOR E. ODLAND, Chairman, Providence, 1948. Mimeographed.

"The committee was authorized to make a study of the processes and equipment necessary to convert sludge and other waste materials (vegetable and animal) into plant food or fertilizers, and all other by-products and base materials for conversion to many practical purposes." The report presents information as to the quantity and quality of sewage sludges, the hygienic aspects of their use, and the problems in their processing. It also deals with garbage, seaweed, starfish, fish waste, oyster shells, wool-scouring waste, slaughterhouse refuse, animal manures from stock cars, brewery wastes, and sawdust and shavings. The committee recommends the appointment of a waste-conversion authority for Rhode Island.

*Soil Conservation, an International Study.* By MARK BALDWIN, ET AL. Food and Agriculture Organization of the United Nations, Washington, 1948. Pp. 189, figs. 95. Bound in paper. Price \$2.

This is an exceptionally well organized, illustrated, and documented presentation of soil conservation as a world problem. The foreward is by John Boyd Orr. The several chapters deal with physical factors, economic factors, physical, economic, and social losses from mismanagement of farm land, shifting-cultivation, range and forest lands, organizing and planning soil conservation projects, and national soil conservation programs. The appendix contains a general bibliography, the conservation acts of the United States and Mexico, the TVA memorandum of understanding, and a schematic land map of the world. The authors are Mark Baldwin, J. Lossing Buck, Herbert Greene, A. B. Lewis, T. C. Tsiang, S. B. Snow, Thomas B. Chambers, J. Gordon Steele, Charles E. Kellogg, and Robert L. Pendleton.

THE EDITORS



# REQUIREMENTS FOR SUCCESSFUL SOIL TESTS<sup>1</sup>

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During the last two decades interest has been renewed in the possibility of using chemical methods and tests to measure the fertility in a soil. The chemists of the nineteenth century made little progress along this line, and their lack of success discouraged such studies for many years. The principal reasons for this lack of progress appear to have been a lack of sufficient knowledge about the chemistry of soil fertility and a strongly held, preconceived idea that the chemical methods should simulate plant feeding and measure the availability of the nutrient. A decade ago, the writer (1) challenged this preconceived idea, pointed out its faults, and set up new concepts as guides for planning research to measure fertility with chemical methods. Rigid adherence to these concepts made it possible later to correlate the phosphorus and potash soil-test values with the percentage sufficiency of the nutrient for each crop studied.

In that paper, the concepts were discussed as follows:

... Usually more than one form of an element occurs in the soil at any one time. Each form contributes to a greater or lesser extent to feeding by plant roots. The significance of each form to the growth of each crop under varying conditions can be established by studies of plant growth and soil chemistry. The form or forms found to be of most significance to the immediate growth of the plant can be measured chemically and this information can serve as a partial basis for treatment recommendations ...

... No attempt is made to measure the composite "availability" of all the forms of a given element present nor is the feeding power of the plant roots simulated in the extracting solution used. Instead, the extracting solutions to be used are those which can extract all of that form or forms of the element being tested for and which have, therefore, a purely chemical basis. ... the methods or tests must not only measure the significant forms of the elements, but also correlations must be established between the amounts of these forms of the elements present and crop response to the fertility elements applied.

A practical test or method is, therefore, one which has been calibrated against actual crop response under the conditions concerned ...

... Such a method should measure these forms quantitatively—at least, roughly so ...

The requirements for a successful soil test, therefore, may be briefly stated as follows:

1. The extracting solution and the procedure used should extract the *total amount* (or a *proportionate part*) of the *available* form or forms of a nutrient from soils with *variable* properties.
2. The amount of the nutrient in the extract should be measured with reasonable accuracy and speed.

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<sup>1</sup> Contribution from the department of agronomy, Illinois Agricultural Experiment Station, Urbana, Illinois. Published with the approval of the director.

<sup>2</sup> Professor of soil fertility.



3. The amounts extracted should be correlated with the growth and the response of each crop to that nutrient under various conditions.

*Requirement 1.* Before one can extract an available form of a nutrient from a soil, one must know which forms are available and the nature of those forms. Is it a form like exchangeable potassium, calcium, and magnesium? Is it an adsorbed form like the phosphate ion, or is it a slightly soluble compound like tri-calcium phosphate?

To develop a soil test, one must first develop a solution which can extract the total amount of an available form or a proportionate part, and this can best be done by first knowing the nature of the available form.

Before we can answer, we must define what we mean by an available form. The writer's definition implied in the aforementioned paper is as follows: *The available forms of a nutrient are those whose variations in amount are responsible for significant variations in yield and response to applied fertilizers.*

This definition excludes any form whose contribution to plant growth during the growing season is relatively insignificant. For example, the writer has found that a concentration of about 150 pounds of exchangeable potassium per 2,000,000 pounds of soil is required for 90 per cent of the yield of corn which is obtainable where potassium is adequate. A release of 20 pounds of potassium in one year from the mineral forms within the rooting area would have little effect on the percentage sufficiency and would not affect the correlation even though it would help to maintain the supply of exchangeable potassium. The mineral forms like the feldspars would not be included, therefore, as significant available forms, even though they were maintaining the supply of available potassium against decline.

Another example is organic (humus) phosphorus. Corn requires about 100 pounds of available phosphorus per acre for a 90 per cent yield. This is the *total* available amount, not the proportionate part measured by the soil test. The release of 10 pounds of phosphorus from soil organic matter can change the percentage yield only very slightly (3). Yet it could be sufficient to *maintain* the supply of available phosphorus. A "low" test on a soil not responding to phosphorus cannot be explained as due to the fact that the organic phosphorus which is released is supporting plant growth and being used as fast as it is released. No relatively immobile nutrient can be used as fast as it is released, because the released nutrient is adsorbed, and grain crops, when planted at the customary rates, can obtain only approximately 5 to 20 per cent of the immobile nutrients present in the rooting area during any one season. In situations where the nature of the available forms is unknown, exacting studies of the chemistry of the soils must be made in addition to the trials of the existing test methods. A prevalent assumption that the chemistry of soil fertility varies widely is not true. When properly classified, soil types should fall into *groups* having chemical properties similar in nature and subject to the same soil-test correlations. For example, in Illinois, for practical purposes, all silt and clay loam soils can be grouped into one group so far as the nature of the chemistry of available potassium and phosphorus is concerned.

*Requirement 2.* Once a good extracting solution is obtained, amounts and ratios of soil and solution are chosen to include the reading range desired. The concentration of the nutrient in the extract must be high enough that small amounts in the soil can be detected by the methods used, and yet not so high as to be outside the significant reading range. As this part of the correlation requirement involves only the application of the principles of chemical analysis and has little to do with soil chemistry, it need only be said that accuracy in this part of the determination is essential.

One problem which often presents itself to the research man is the possibility of saving time by running more than one test on the same extract. If requirement 1 is met for all the nutrients to be run in the extract, well and good. But to sacrifice accuracy to the point where good general correlations can no longer be obtained, just to reduce the cost of running the tests, defeats the whole purpose of soil testing. It is true, however, that poorly elaborated solutions can be correlated for very specific conditions and can be of some value as long as their use is restricted to those conditions.

But the history of soil testing shows that such restrictions are not upheld or, in some cases, even recognized as necessary. For example, the extracting solution suggested by Morgan as a "universal" soil-extracting solution so violates requirement 1 that the term "universal" is an unfortunate designation. The amount of phosphorus extracted by this solution gives no idea of the relative amounts present in the significant range for most soils and crops. As used by most advocates, the potassium test is also highly inaccurate, not because of the chemical determination of the potassium in the extract, but because of the inability of the extracting solution to extract either the total or a proportionate part of the exchangeable potassium from soils varying in exchange capacity.

*Requirement 3.* The correlation of the soil test value with crop needs and response is the final requirement.

If we have met requirements 1 and 2 we can measure the available form or forms of a nutrient. Now we must ask the plant what each amount of each form means to it. To find this out requires certain experimental data obtained in the field under the conditions to which the final correlation will be applied. To find out how deficient in a certain nutrient a soil is, one must apply adequate amounts of that nutrient so that it no longer limits yields. But it should be applied *under conditions where other nutrients are not limiting yields*. The check plot should be a plot where all nutrients but the one being studied are adequate. In the treated plot, all nutrients including the one being studied should be adequate. The magnitude of the yields and the difference between them is the crop's measure of the deficiency of that nutrient in the check plot. The soil-test value for that nutrient in the check plot is the amount which produces the deficient yields found. If these two plots are adjacent, the effect of other variables is reduced to a minimum, and virtually the only thing that will cause these two yields to vary widely will be a deficiency of the nutrient in the check plot. If the plots are separated and randomized, other variables are intensified, and the accuracy of the correlation is reduced correspondingly.

The above procedure gives three values; the yield ( $y$ ) without added quantities of the nutrient, the yield ( $A$ ) with the nutrient adequate, and the soil-test value ( $b_1$ ) of the plot not receiving the nutrient.

Mitscherlich and Baule found that the relationship between these three values could be expressed as

$$\text{Log } (A-y) = \log A - c_1 b_1,$$

where  $c_1$  is the proportionality constant.

The writer has confirmed this for exchangeable potassium and the adsorbed and easily acid-soluble forms of phosphorus for the soils of the corn belt (2, 3).

Where such a relationship holds, the problems of soil-test correlations are greatly simplified. Theoretically, only three values are needed to establish the value of  $c_1$ , for a given rate of planting, and once  $c_1$  is found, any value of  $b_1$  can be interpreted in terms of its percentage sufficiency by letting  $A$  represent the 100 per cent yield where the nutrient is 100 per cent sufficient, that is, adequate. This reduces all productivity levels to a common denominator, the percentage yield or percentage sufficiency, and permits the calculations of the percentage sufficiency of  $b_1$ . The  $c_1$  value is a constant for the crop grown and its planting rate. Different crops and different planting rates may be expected to change the  $c_1$  value.

One cannot take for granted, however, that all the soil conditions in any large area will give a constant  $c_1$  value. These adjacent pairs of plots should be randomized throughout the area to which the correlation is to be applied. Soils varying widely in physical and chemical characteristics and in productivity should be used. Parallel with this, the soils should be selected to represent a wide range of soil-test values, that is, available nutrient contents. The number of pairs of plots on a single field should be restricted in favor of a greater number of fields.

Using this method, Arnold and Schmidt<sup>3</sup> were able to obtain in one year a practical tentative correlation between the writer's phosphorus test and the soil requirement of tomatoes for phosphorus. Farm fields were used, and the procedure followed was the same as would be subsequently followed in applying the correlation. A second and third year's work on other fields, representing other soil conditions, verified the first year's correlation. Such a procedure gives the correlation between the amount of an available form present and its sufficiency for crop growth in terms of percentage, which is the most valuable correlation for practical use because it enables one to regulate fertilizer applications so that neither too much nor too little is permitted to accumulate in the soil. One does not have to know the exact phosphate fertilizer requirement, since any excess fertilizer which is applied only serves to build up the available soil phosphorus, and the accumulation of excess fertility in the soil can be avoided by a soil-testing program.

If one desires a more exact fertilizer requirement, for a given method of fer-

<sup>3</sup> Arnold, C. Y., and Schmidt, W. A. Unpublished data. Ill. Agr. Exp. Sta., Dept. of Hort. and Campbells Soup Co., cooperating, 1947.

tilizer application, extra plots treated with increasing increments of the fertilizer form of the nutrient can be included with the above pairs. They should be adjacent to the sides and corners of the check plot.

Fewer randomized replications of this block of plots on various soil conditions are needed but they should especially include extremes in productivity and in the chemical and physical nature of the soil. The data obtained are analyzed through use of the following equation:

$$\text{Log } (A-y) = \text{log } A - (c_1b_1 + cx),$$

where  $x$  is the amount of the fertilizer form added,  $c$  is the unknown proportionality constant, and  $c_1$  has already been found by solving the first equation (3).

When both  $c_1$  and  $c$  are known, one can test a soil in the area where the correlation is known to hold and can tell the farmer his possible percentage increase in yield and the amount of fertilizer needed to obtain it, provided the other factors in crop growth are sufficiently favorable.

The soil test for phosphorus or potassium tells only the status of those nutrients. A low test may not mean that fertilizer should be used. Any practical *recommendations* for the use of phosphate or potash must be based not only on the knowledge obtained from these tests but also on knowledge concerning the favorableness of the other factors in crop growth.

#### DISCUSSION

The above outline should not necessarily be followed in a stepwise fashion. To find the nature of the available forms, plant studies as well as the chemical studies can be made simultaneously. The relative significance of the different soil forms might be judged from their chemical nature, but plant growth and response must be the final criteria. This means that soils of known variation in response are needed for the chemical studies of those nutrient forms contributing to the variations in response. It is only after these preliminary studies have been made that an extracting solution can be devised.

The nature and the utilization of exchangeable potassium by plants were already well known before soil tests were devised. All that remained to be done was to eliminate other forms as possible significant contributors to crop response. In corn-belt soils no other forms were found to be of immediate significance to the growing plant. The exchangeable potassium values were found to be closely equivalent to the Neubauer values, indicating no significant release from other forms during the growing season. This was, of course, verified by the high degree of correlation found between exchangeable potassium and crop response data in the field experiments. The possibility that release from "difficultly exchangeable" or other forms might be significant under some conditions must not be ignored, and will automatically be brought to light if the proper preliminary studies have been made.

The problem of available phosphorus is more difficult than that of available potassium because more than one form occurs in significant amounts and each form, varying in amount as well as insolubility, must be measured. In corn-belt



soils the adsorbed and easily acid-soluble (calcium) forms predominate. Small amounts of the adsorbed forms are less "soluble," pound for pound, than small amounts of the calcium forms. But as the adsorbed forms increase, their solubility in water increases and surpasses the more constant solubility of such a form as tricalcium phosphate. The adsorbed and calcium forms are in equilibrium with each other, and the higher the pH, the greater the proportion of the calcium forms. It is obvious, therefore, that in the case of phosphorus the correlation cannot be expected to be as exact as where only one form is being measured. For corn-belt soils, the acidity of the writer's extracting solution and its fluoride concentration were adjusted so that somewhat proportionate amounts were being extracted even though the total amounts were not. A good correlation was obtained (3).

The mobility concept recently put forth (4)<sup>4</sup> leads to the conclusion that only the relatively immobile nutrients like phosphorus and potassium can be made the subject of the type of correlation described above. According to this concept, only the relatively immobile nutrients follow the Baule percentage yield relationship over a wide range of productivity. Nutrients, like mobile nitrate nitrogen, which are soluble and can move to the plant roots have a more nearly absolute relationship to the yield possibility, similar to Liebig's "law of the minimum." For example, a certain amount of a relatively immobile nutrient may be just sufficient for 80 per cent of either a 25-bushel yield of corn or a 100-bushel yield of corn. But a certain amount of a mobile nutrient like nitrate nitrogen, which approaches 100 per cent availability, is good for a certain yield, with only a very narrow possible variation. The reasons for this are fairly obvious.

This situation means that soil-nitrate needs, as contrasted to phosphorus and potassium needs, vary much more with the other factors in productivity. As a result, the tissue test for nitrogen is a more reliable indicator of the plant's needs than are soil tests.

The mobility concept in soil fertility, according to which only the relatively immobile nutrients follow the Baule percentage yield relationship, would indicate that, if two such nutrients were deficient, they would both remain deficient and should test "low" in the plant tissue as long as other nutrients are adequate. If a mobile nutrient like nitrate nitrogen were deficient, however, they could both accumulate and give "high" tests even though they, also, were deficient. If this is true, the tissue test for nitrate should give a good indication of the nitrogen situation because it is probably the only really mobile soil nutrient, other than water, and the rest of the nutrients follow the Baule percentage yield relationship. Thus, only where the nitrate tissue test is positive would the potassium or

<sup>4</sup> Bray, R. H. Soil nutrient status as related to the responses and yield of crops. Paper given at the St. Louis meeting of the American Association for the Advancement of Science, March, 1946. Unpublished.

Bray, R. H. The nature of a fertile soil. Address given at the Twenty-Sixth Annual Banquet, Kentucky Chapter of the Society of Sigma Xi, 1947. Unpublished.

Bray, R. H. Certain factors to be considered in corn fertilization. Paper given before the Soil Science Society of America, 1948. Unpublished,



phosphorus tissue test be a good indicator of deficiency of potassium or phosphorus in the soil. This deduction has not yet been completely verified.

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## STRUCTURAL VARIATIONS OF YANGAMBI (BELGIAN CONGO) SOILS

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The soils at Yangambi have developed under a climax vegetation of tropical rain forest (1). They have mature profiles with relatively uniform characteristics over a considerable area. These soils have probably reached a state of equilibrium with the factors that formed them. When the forest is removed, at least two important soil-forming factors—climate and vegetation—are materially modified. The disturbance of the equilibrium prevailing under the rain forest is immediately reflected in an accelerated change of several soil characteristics. This is particularly true if food crops are grown. After a 3-year rotation of food crops, the soil needs a fallow, which naturally culminates in a semipermanent association of *Musanga smithii* R-Br. At this stage, the changes become less marked and the soil approaches a new equilibrium, different from that under the climax vegetation.

Yangambi is the principal research station of the Institut National pour l'Étude Agronomique du Congo Belge (I.N.E.A.C.) in Africa at 0° 45'N and 24°29'E. The elevation is about 470 m. The station is located on a plateau dominating the right bank of the Congo River and is bordered by steep cliffs about 50 m. high. The cliffs show a succession of sandy and clayey slightly consolidated sediments in concordant and subhorizontal stratification. The average annual precipitation is 169 cm.; the average annual temperature is 24.5°C., and the average annual maximum temperature is 30.3°C., with a corresponding minimum of 18.7°C. The average temperature of the soil at a depth of 75 cm. is 26.3°C.<sup>1</sup>

The three characteristics of the soil that have proved to be representative, sensitive, and subject to relatively large variations when the equilibrium is disturbed are (a) the specific surface, (b) the total colloid content, and (c) the content of naturally peptized colloid. The first of these is a function of the soil structure and is very closely related to the other two. The last characteristic is closely related to the vegetation.

### VEGETATION AS A PEPTIZING FACTOR

The colloidal fraction of the soil can be present in either a peptized or a flocculated state. An easy test can be made to determine which of the two forms predominates in a particular soil sample. A soil profile near Yangambi has the following successive horizons:

<sup>1</sup> A more detailed report, entitled "Recherches sur les variations de structure des sols à Yangambi (Congo Belge)," is to be published soon by I. N. E. A. C., Rue aux Laines 12-14, Brussels.

1. An upper horizon having mostly peptized colloid.
2. A transitional horizon in which the degree of peptization is much less.
3. A continuous horizon where all of the colloid is flocculated.

Plant activity has been found to be the principal cause of this peptization phenomenon. This is evidenced by the fact that soil adhering to plant rootlets always has the greater part of its colloid peptized. This is most striking with young plants that are getting a foothold where the soil colloid is entirely flocculated (for example, on the wall of an old profile pit). Another evidence of the effect of plant materials is the fact that a water extract of forest litter will peptize the flocculated soil colloid. It is also noted that plant growth on the cliffs of Yangambi has a marked effect on their susceptibility to erosion. The chief cementing agent in the soils found on these cliffs appears to be strongly flocculated clay. The greater mobility of the peptized clay in the neighborhood of vegetation strongly favors erosion.

The mechanism of the direct or indirect action of vegetation is not quite clear. It is observed, however, that the colloidal behavior of flocculated and peptized soil colloids is quite different. The flocculated soil colloid can be regarded as a discharged suspensoid, and the peptized colloid, as an emulsoid. The low pH values (3.5 to 4.5) and the hydroxide coating of the particles readily explain their flocculated state. The naturally peptized soil colloid also maintains its stability in an acid medium (pH 3.5 to 4.5). Because it is sensitive to the action of dehydrating agents like alcohol, the main stabilizing factor must be hydration, a characteristic of emulsoids. A flocculated soil colloid can be peptized by the addition of small amounts of emulsoids like agar-agar dextrine and gum tragacanth. Substances like butyric acid which are effective in changing surface tension can modify the degree of flocculation. Glycerine, mannitol, and even certain anions, such as the citrates and lactates, greatly increase the volume of the flocculate. All these substances have one feature in common: they are strongly hydrated. The outer coating of highly hydrated substances explains the natural peptization in an acid medium and the emulsoid character of the colloid.

It is observed that peptization is most marked in the vicinity of rootlets. There we find the root hairs whose ephemeral existence assures a constant supply of raw organic material. This area is identical with the rhizosphere of Hiltner (9), a zone that is subjected to root excretions and that is the seat of intense microbiological activity. It is quite reasonable that in the immediate neighborhood of the rootlets certain substances should be formed, colloidal or otherwise, that are highly hydrated and subject to absorption on the colloid surfaces.

The peptization phenomenon was studied systematically in the field in trenches that were dug 40 m. long and 1.5 m. deep. At intervals of 1 m. the dispersion of the colloid was determined along a vertical section. For this purpose the following quick test was used: Two to 5 gm. of fresh soil is thoroughly mixed with 1 ml. of a reagent consisting of a freshly prepared 20 per cent (by volume) solution of  $\text{CCl}_4$  in  $\text{CH}_3\text{OH}$  in a large test tube. Then 50 ml. of distilled water is added,

and the tube is agitated and left for a few minutes. The beginning of flocculation (the under limit of the peptized layer) and total flocculation can be easily located in the soil. It is noted that microrelief, different vegetative matter, and termite mounds have a marked influence on the depth of the peptized zone. If it is desired to isolate the action of living plants, these other effects may be considered as accidental and can be eliminated by statistical study. The quick test observations are first plotted to scale on a graph of the trench wall. Three such zones are traced in figure 1.

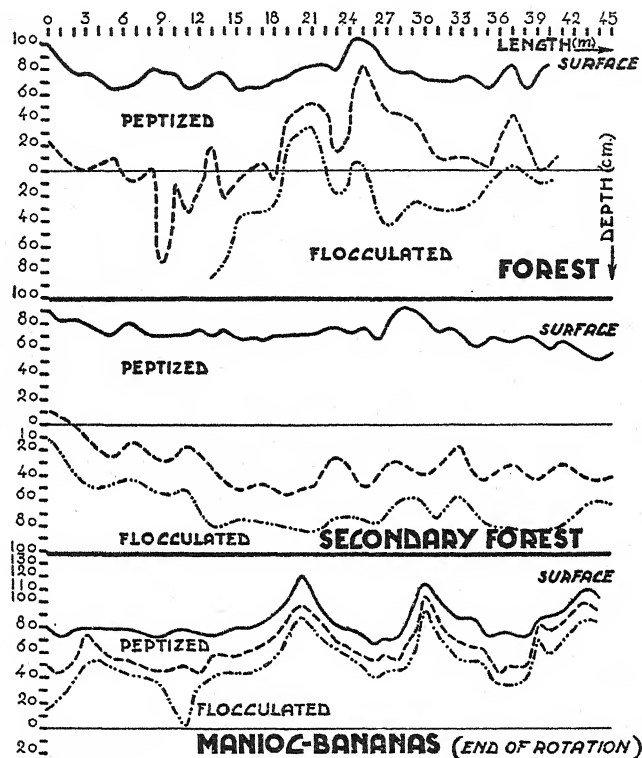


FIG. 1. DISPERSION OF PEPTIZED AND FLOCCULATED COLLOIDS IN THREE ZONES AS INDICATED BY GRAPHS OF TRENCH WALLS

The depth of the peptized layer is measured at frequent regular intervals in order to trace a frequency-intensity curve. A comparison of the curves obtained by examination of different trenches (fig. 2) shows that most of these curves have well-marked maxima corresponding to typical peptization depths. It is found that the maxima often occur at the same depths for different trenches. Because these depths are closely related to plant root systems, typical maxima may indicate characteristic plants or plant associations. Observations are not yet numerous enough to establish this point. A study of the trench graphs makes possible the choice of the most representative profiles for sampling for additional studies.



## SPECIFIC SURFACE AS A MEASURE OF SOIL STRUCTURE

If parts of the same soil sample are sieved after intervals of several days, it is found that the weight of the fraction passing through may vary greatly. Further desiccation may bring about crumbling of the coarser aggregates. The properties of the finer fraction, however, remain fairly constant. This suggests the presence in the soils of structural units or fabric units (6) of relatively great stability. The specific surface appeared to be a good measure for evaluating

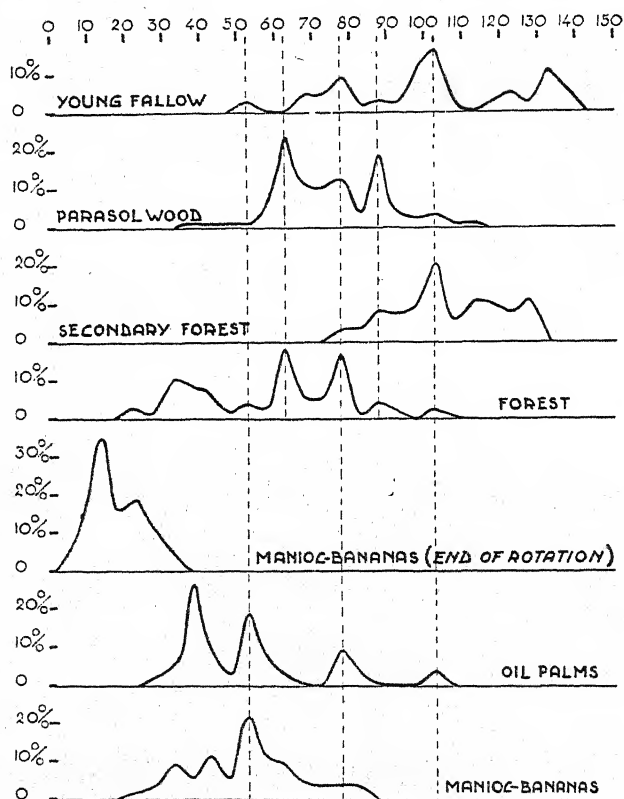


FIG. 2. FREQUENCY-INTENSITY CURVES OF DEPTHS OF PEPTIZED LAYERS IN DIFFERENT TRENCHES

Abscissa represents depth of peptized layer in centimeters. Ordinate represents frequency.

these structural units. It can be defined as the total surface exposed in 1 cc. of the soil material. This is a measure of both permeability and porosity and gives precise figures. The specific surface is also an additive value. This is important because the specific surface of the coarser fractions may be disregarded, and from the percentage of the analyzed fraction an evaluation of the specific surface of the whole soil can be made. All examinations were made on the fraction of soil passing through a sieve of 0.297-mm. mesh.

The method employed for specific surface measurement is based on the work

of Sullivan and Hertel (5). The apparatus employed is shown diagrammatically in figure 3. In operation a flow of air is forced through a column of dry soil material. The flow of air  $\Delta Q$  and the pressure difference between the top and bottom of the soil column are also measured. These values are related by the following formula:

$$\Delta Q = \frac{A}{\mu S_0^2} \cdot \frac{1}{K} \cdot \frac{1}{L} \cdot \Delta P f(\epsilon)$$

where  $f(\epsilon) = \frac{\epsilon^3}{(1 - \epsilon)^2}$ ;  $\Delta Q$  = air flow;  $A$  = section of soil column;  $L$  = length of soil column;  $\Delta P$  = pressure difference;  $\mu$  = air viscosity;  $S_0$  = specific surface;  $\epsilon$  = porosity;  $K$  = constant.

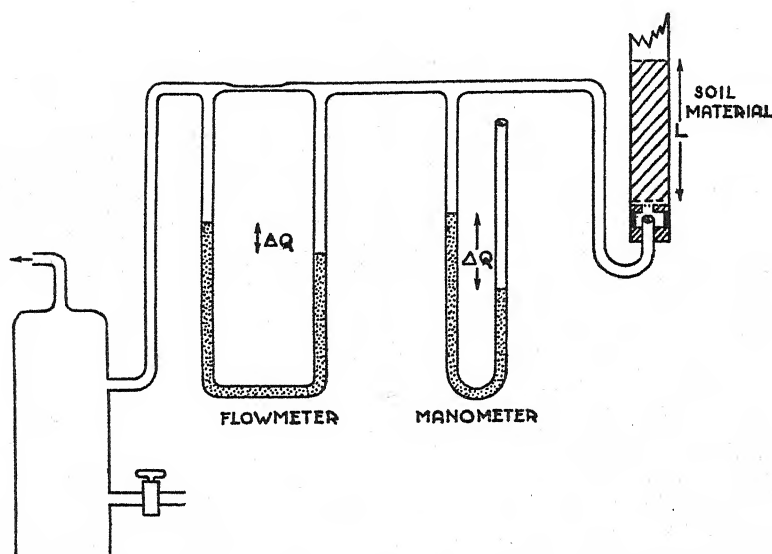


FIG. 3. APPARATUS FOR MEASURING SPECIFIC SURFACE OF SOIL MATERIAL

This formula can be simplified as follows:  $\mu$ ,  $K$ , and  $A$  can be combined into one constant; since  $\Delta Q$  is related by linear function to  $\Delta P$ , both factors can be replaced by an angular coefficient; and within the limits of our work,  $\log f(\epsilon)$  is a linear function of  $\rho$ , where  $\rho = \frac{\text{weight of sample}}{2.65} \times \frac{1}{L}$ .

Specific surface generally varies within the soil profile as follows:

1. It is low at the surface.
2. It passes quickly through a maximum, found at variable depths for different vegetations and treatments.
3. It decreases slowly.
4. It fluctuates around an average value.

## TOTAL AND PEPTIZED COLLOID CONTENTS AS TWO FACTORS OF SOIL STRUCTURE

The fundamental differences between peptized and flocculated soil colloids were discussed earlier in this paper. To study correlations between structure and colloid content, it is necessary to start with determination of the two colloidal forms. Furthermore, only the colloid whose flocculation is reversible under natural soil conditions is determined. It is not to be expected that irreversible flocculates, such as pseudosands, should contribute to soil structure in the same manner as clay. Therefore, the normal dispersion methods, especially those involving the use of hydrogen peroxide and hydrochloric acid-alkali, cannot be employed.

A new dispersion method has been devised, the action of which goes no further than the water links [Russel (7) theory] and which is based on surface phenomena. The reagent employed is a freshly prepared 20 per cent (by volume) solution of carbon tetrachloride in methyl alcohol. Ten to 20 gm. of air-dry soil is placed in a large dry test tube and moistened with approximately 5 ml. of this reagent. After gentle shaking for a few seconds, a sticky paste is formed. Then 50 ml. of distilled water is added and the suspension is shaken violently four or five times. After standing 1 minute the suspension is decanted into a hydrometer jar. The residue is reshaken two or three times with fresh distilled water until the sand is clean and the supernatant liquid in the test tube remains clear. The hydrometer jar is then filled and the colloid content is measured by the Bouyoucos-Casagrande method (2, 3). This gives the peptized colloid content. The flocculated particles recoagulate and settle, whereas the peptized colloid remains in suspension.

The method is based on the following examinations regarding the mechanism of the reactions:

- a. Methyl alcohol in contact with the water films coating the particles dissolves in the water. The result is a partial dissolving and a decrease of the interfacial tension between  $\text{CCl}_4$  and water.
- b.  $\text{CCl}_4$  is drawn into the water films, spreads on the water, and destroys cohesion.
- c. A partial, spontaneous emulsification of  $\text{CCl}_4$  causes an orientation of liberated particles in the contact layers between  $\text{CCl}_4$  and water.

After dispersion, the flocculated fraction having the maximal surface compatible with its state can easily be peptized completely by successive additions of small quantities of electrolytes such as ammonia.

The suspension is decanted several times into a hydrometer jar, and measurement gives the total colloid content. Hydrometer readings are made after a settling time of 45 minutes. Under the given tropical working conditions, this settling time corresponds to a maximum particle diameter of  $8\mu$ . In this manner the following values are obtained:

$P$  = percentage of peptized colloid in soil

$T$  = percentage of total colloid

$F$  = percentage of flocculated colloid

$$F = T - P$$

$\frac{P}{T} \times 100$  is called the degree of peptization.

Figure 4 gives a schematic representation of  $T$ ,  $P$ ,  $F$ , and  $\frac{P}{T} \times 100$  variations in the profile.

The highest root activity is localized in the neighborhood of point 2. Point 3, the maximum of the peptization curve, is generally somewhat lower than point 2 in mature profiles. In younger profiles the  $F$  minimum and the  $P$  maximum are not so well marked. Point 4 corresponds to the lower limit of the peptized zone already mentioned. These curves also show great differences for soils under different vegetative conditions.

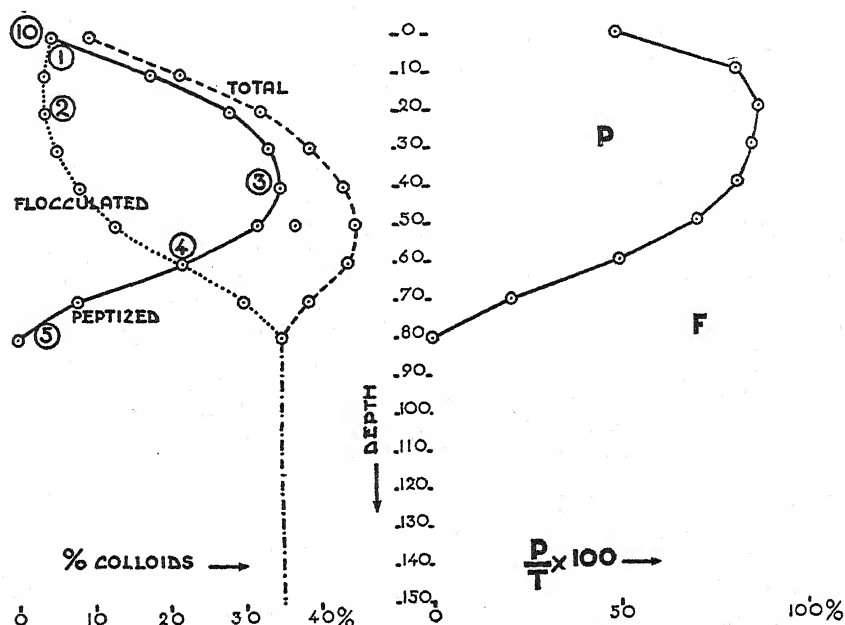


FIG. 4. SCHEMATIC REPRESENTATION OF VARIATIONS OF PERCENTAGE OF TOTAL COLLOID ( $T$ ), OF PERCENTAGE OF PEPTIZED COLLOID ( $P$ ), OF PERCENTAGE OF FLOCCULATED COLLOID ( $F$ ), AND OF DEGREE OF PEPTIZATION ( $\frac{P}{T} \times 100$ ) IN THE PROFILE

#### MEASUREMENT OF SOIL STRUCTURE

##### *Specific surface as a mathematical function of peptized and flocculated colloid content*

In each profile, a layer where all peptized colloids have disappeared occurs at some depth ( $P = 0$ ). In general, the following equation applies:

$$T = P + F. \quad (1)$$

A large number of soil samples taken at random over an area of 250 sq. km. were analyzed. The upper horizons of the profiles from which these samples were taken bore primeval forest, plantations, food crops, or fallow. The samples were grouped into 3 per cent compartments according to their total colloid content.

The specific surfaces ( $S_0$ ) of the samples of each 3 per cent group could be differentiated into two distinct subgroups: the first had very high  $S_0$  values; the second had lower ones. The average  $S_0$  values of each subgroup were plotted against the total colloid content and gave two distinct linear functions (fig. 5).

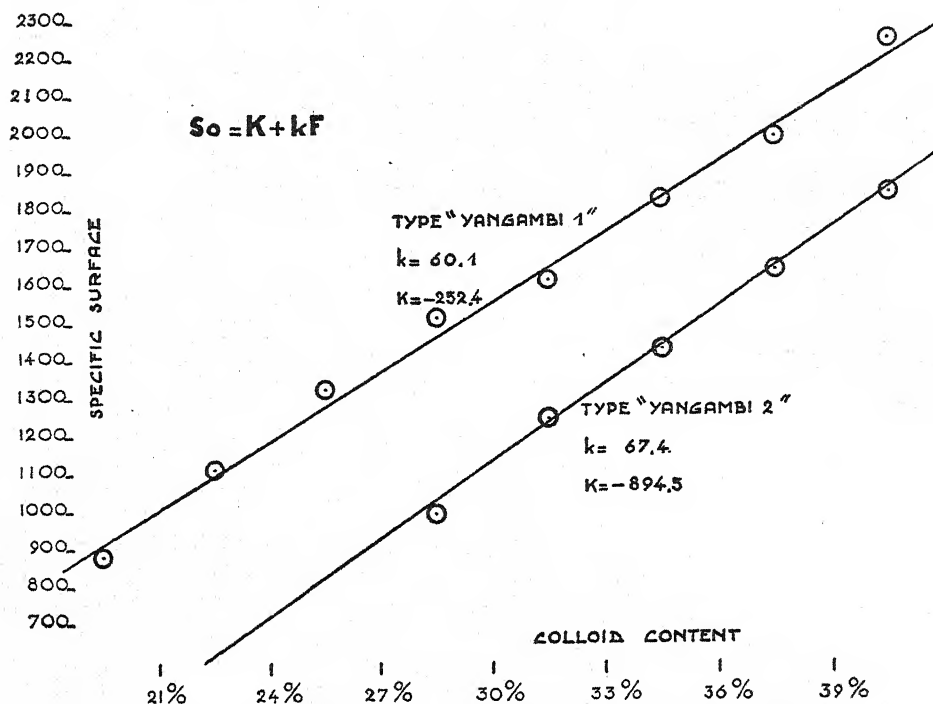


FIG. 5. LINEAR FUNCTIONS BETWEEN SPECIFIC SURFACE AND TOTAL COLLOID CONTENT

The analytical equations for these two linear functions can be written in the following form:

$$\begin{aligned} S_0 &= K + kF \\ S_0 &= K' + k'F, \end{aligned} \quad (2)$$

where  $K$ ,  $K'$ ,  $k$ , and  $k'$  are constant values.

The constancy of these two subsoil characteristics under most different vegetations seems to indicate that the influence of the vegetation on the structure must have ceased there, and that  $K$  and  $k$  are dependent on parent material. According to these equations,  $K$  can have negative values; however, since  $S_0$  cannot become negative,  $kF$  must always be greater than  $K$ . Two explanations of this consequence are possible: either the validity of the equation is limited, or for a given soil type the colloid content of its structural units does not fall below a certain limiting value. It has not been determined which of these two explanations is correct.



In the upper horizons where the soil colloid is partly peptized, equation (2) does not hold. This is to be expected because the influence of peptized colloid on structure is quite different from that of flocculated colloid. In these upper horizons,  $S_0$  is a function of  $P$  in addition to the terms used in equation (2). The following empirical equation proved to be applicable:

$$S_0 = K + k F + \kappa \frac{P}{T} \times 100. \quad (3)$$

The term  $\kappa$  will be explained in more detail later. In the subsoil horizons  $\kappa \frac{P}{T} \times 100 = 0$ , and  $S_0 = K + k F$  [equation (2)].

TABLE 1  
Calculation of the  $\kappa$  values in three different soil profiles

DEPTH	$T$	$P$	$\frac{P}{T} \times 100$	$S_0$	$k$	$K$	$\kappa$	AV. $\kappa$
cm.								
0-10	15.0	7.9	53.3	1029	60.1	-252.4	16	15.7
10-20	29.9	10.6	35.5	1445.6			15.2	
20-30	30.4	22.8	74.9	1394.7			15.9	
0-15	25.9	14.4	55.8	1806	60.1	-252.4	24.6	25
15-30	33.6	26.0	77.4	2155.8			25.3	
30-45	36.6	5.2	13.3	2234			25.0	
0-10	29.0	11.4	39.3	1349.3	67.4	-894.5	26.9*	20.5
10-20	28.2	16.6	58.9	1145.7			21.4	
20-30	27.3	17.4	63.7	1128.6			21.3	
30-40	27.7	20.2	73.0	1071.7			20.0	
40-50	28.4	6.9	24.3	1023.7			19.3	

\* This value should be excluded. Surface samples sometimes give aberrant results due to their organic material content and lower specific gravity. This affects both  $S_0$  and colloid content determinations.

To establish the validity of equation (3), 30 soil profiles were studied. Between the surface and the lower limit of the peptized zone the soil profile wall was divided into horizontal layers 10 cm. wide.  $S_0$ ,  $T$ , and  $P$  were determined for each layer. The corresponding subsoil samples gave values for  $K$  and  $k$ . From these five values,  $\kappa$  could be calculated for each sample. These calculations are illustrated by the three profiles in table 1.

$\kappa$  remains fairly constant in the profile, whereas the other factors vary greatly.

When comparisons are made of soils covered by the same type of vegetation and subjected to identical agricultural treatment, the constancy seems to be maintained. For example, three profiles taken 15 m. apart under a 3-year-old fallow gave the following average  $\kappa$  values: 14.9, 16.6, and 15.3.

*Interpretations of equation (3)*

$S_0$  can be considered as the sum of two distinct functions:

$$\begin{aligned}\phi F &= (K + k F) \\ \phi P &= \left(\kappa \frac{P}{P + F} \cdot 100\right)\end{aligned}$$

and

$$S_0 = \phi F + \phi P.$$

$\phi F = (K + k F)$ . The flocculated colloids are present in variable quantities, but they also have different qualities. Colloidal properties are essentially surface properties, and these are greatly influenced by modifications of the particle coatings. The qualities of the flocculated particles are, in the first place, conferred on them by the parent material. There may be different types of flocculated colloids, and each type forms different structural units. The quality of the flocculated colloids is reflected by  $K$  and  $k$ . It is quite logical, therefore, to distinguish soil types by their  $K$  and  $k$  parameters as given in equation (3). This has been done in figure 5, where a distinction is made between the two linear functions called "Yangambi 1" and "Yangambi 2."

$\phi P = \left(\kappa \frac{P}{P + F} \cdot 100\right)$ . If a flocculated soil colloid is peptized by biological action, it acquires new properties. These are functions of the biological factors which dispersed it and of the qualities inherent in the flocculated colloid. Now we can distinguish the notions of *intensity* and of *quality*. The intensity of peptization is given by the degree of peptization,  $\frac{P}{P + F} \cdot 100$ , whereas the quality depends on two series of causes: those deriving from the qualities of  $F$ , that is, the parameters  $K$  and  $k$ ; and those inherent in the mechanism of peptization. The quality is expressed by  $\kappa$ . It represents a biological action on a given type of flocculated soil colloid.

Equation (3) can be written in another form:

$$S_0 = (K + k T) + \left(\frac{100\kappa}{T} - k\right) P,$$

and the two terms can be studied separately:

$(K + kT)$ —groups of factors not affected by cultivation; these are colloid content and flocculated colloid quality.

$\left(\frac{100\kappa}{T} - k\right) P$ —factors affected by cultivation.

$P$ —plant rootlets peptize flocculated colloids with different intensity. A systematic study reveals the specific activities of different plants.

$\kappa$ —plants must exert a specific influence on the structural quality of peptized colloids. It is by varying this  $\kappa$  value that we can influence the soil structure most effectively. Also, these specific influences can be systematically studied.

When  $S_0$  is considered as an explicit function of  $T$  and  $P$ , two partial derivations can be made:

$$\frac{(\partial S_0)}{(\partial T)} P = k - \frac{100\kappa P}{T^2}$$

and

$$\frac{(\partial S_0)}{(\partial P)} T = \frac{100\kappa}{T} - k.$$

Let us define  $\frac{(\partial S_0)}{(\partial T)} P$  as the "mode of aggregation."

When  $P = 0$  the mode of aggregation is  $k$ , and this means that in all soils of the same type the mode of aggregation of the structural units is the same if no peptized colloids are present.

$\frac{(\partial S_0)}{(\partial P)} T$  can be defined as the "aggregation capacity." It is dependent on  $k$  (quality of the flocculated soils) and on  $\kappa$  (quality of the peptized colloids). It may be positive or negative and its absolute value varies in the profile.

Jenny (4) and others have listed the following independent variables as factors of soil formation: climate, organisms, topography, parent material, and time.

It has been observed that the effect of the factor "organisms" consists principally in peptization of the soil colloids. The intensity of this activity is given by  $\frac{P}{T} \cdot 100$ ; the quality is measured by  $\kappa$ .

The separation of the function  $S_0$  into  $\phi P$  and  $\phi F$  permits the separation of the soil-forming factors into two groups:

$$\begin{aligned} \phi F \text{ implicates } & \begin{cases} \text{Climate} \\ \text{Topography} \\ \text{Parent material} \\ \text{Time} \end{cases} \\ \phi P \text{ implicates } & \begin{cases} \text{Organisms } \begin{cases} \text{microclimate} \\ \text{cultural methods} \end{cases} \\ \text{Time} \end{cases} \end{aligned}$$

#### PRELIMINARY RESULTS

Since the principal aim of this paper is to indicate methods that will give exact and significant values in the study of structural variations in tropical soils near Yangambi, the following results are given primarily for illustrative purposes. Data obtained so far are not numerous enough to warrant general conclusions.

A block of 600 hectares of forest was examined previous to cultivation. Fifty subsoil samples were taken and determination made of the soil type to which each belonged. Sixty-four per cent were of the Yangambi 1 type, 25.5 per cent were of the Yangambi 2 type, and 10.5 per cent were from a different type that was called "Yangambi 3." Later more samples of this type were found. The results are shown in figure 6.

The sand fractions of the samples showed no marked mineralogical differences,

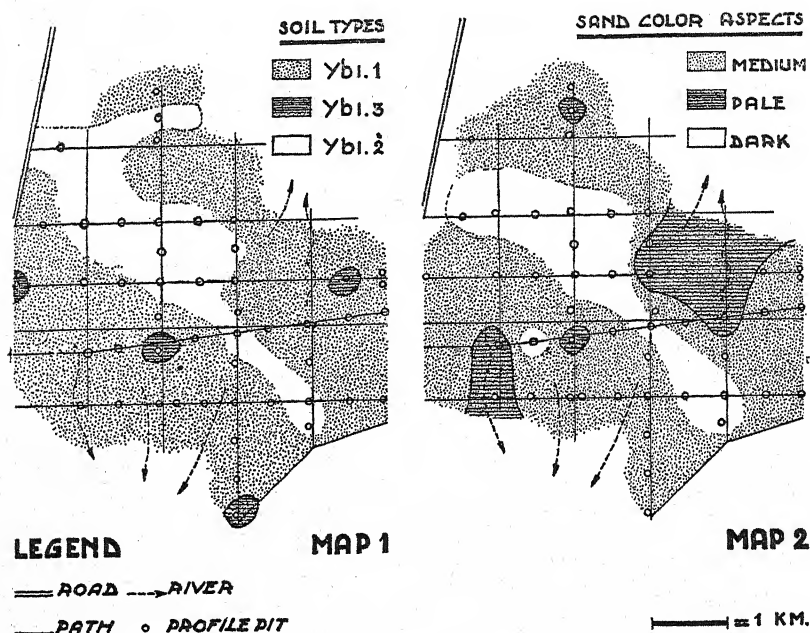


FIG. 6. DISTRIBUTION OF COLLOID TYPES AND SAND COATINGS IN AN EXPERIMENTAL BLOC (PRIMEVAL FOREST) AT YANGAMBI

TABLE 2  
Relation between soil use and the  $\kappa$  value

$\kappa$	DESCRIPTION (YANGAMBI 1 TYPE)	NUMBER
34.9	Primeval forest (cynometra)	1
27.0	Soil under <i>Paspalum notatum</i> fallow for 2 years. Has been under food crops; treated for 7 years by European-inspired cultural methods; other fallow experiments ( <i>Pennisetum</i> , <i>Leguminosae</i> ) failed during 5 years.	2
17.6	Primeval forest where most big trees were felled	3
16.1	<i>Paspalum conjugatum</i> fallow for 2 years. Bears also <i>Erigeron</i> . Old food crops field-cultivated for 2 years. Fallow experiment with <i>pueraria</i> failed.	4
15.7	Forest soil after 2 years of food crops. Bears bananas and manioc.	5
15.6	Forest fallow 2 years old; succeeds 3 years of food crops	6
15.4	Secondary undergrowth; 2 years old, never cultivated	7
14.7	Parasol wood ( <i>Musanga smithii</i> R.Br.) 15 years old	8
13.8	Young secondary forest ( $\pm$ 35 years)	9

but they could be classified according to their color. The following groups were distinguished: red-brown, yellow-brown, and yellow. These groups were also recorded on a map. It was found that the red-brown sand group almost coincided with the flocculated colloids of the Yangambi 2 type. An explanation of

this relation is that the difference in color of the sands is a result of differences in their coating. The quality factors  $K$  and  $k$  must be highly dependent on them. A few exceptions, especially on slopes, may be explained by the possible creeping of the more mobile colloids.

Some results obtained on the Yangambi 1 type are assembled in table 2.

The normal agricultural succession in Yangambi is as follows: primeval forest; cultivated crops (food crops); fallow, *Musanga smithii* (parasol wood); secondary forest.

A comparison of Nos. 6, 8, and 9 (table 2), a fallow-secondary forest succession, reveals that  $\kappa$  gradually decreases. The beginning (primeval forest) and the end point (secondary forest), Nos. 1 and 9 of the table, have respectively the highest and the lowest  $\kappa$  values. The *Paspalum notatum* fallow (No. 2, table 2) has a  $\kappa$  nearest to that of the original forest. A rapid decrease of the  $\kappa$  value is noted when a comparison is made of the primeval forest, the cleared primeval forest, and the young forest fallow (Nos. 1, 3, and 6 in the table). Only systematic research can reveal which  $\kappa$  values are the most favorable for agricultural purposes. However, the equation  $\frac{F}{T} \times 100 = S_0$  presents a certain analogy with the structural factor of Vageler-Alten (8). It is also possible to write  $\frac{P}{T} \times 100 = 100 - S_0$ , and  $\phi P = \kappa (100 - S_0)$ . Vageler and Alten report that soil structure is best when  $S_0$  is nearest to 100. If this is true, a soil under primeval forest presents the less favorable structural properties. The secondary forest is by far the better, as it has a much lower  $\kappa$  value.

#### SUMMARY

It has been observed that plant rootlets exert a peptizing action on flocculated soil colloids.

A method is described for determining the peptized and flocculated colloid content of soils without altering the natural properties of the colloids. The reagent used is a 20 per cent mixture of carbon tetrachloride in methyl alcohol.

The specific surface ( $S_0$ ) of the fraction  $<297\mu$  is considered as a measure of the structural units of the soil.  $S_0$  is calculated from the permeability for air.

A mathematical correlation between  $S_0$  and the peptized and flocculated colloid content of the structural units was found.

The equation makes possible a distinction between different soil types. Moreover, it contains a constant  $\kappa$  that measures the action of vegetative associations on a given soil colloid type.

The techniques have been used to study the fallow problem, and some preliminary results are given.

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# POROUS PLATE APPARATUS FOR MEASURING MOISTURE RETENTION AND TRANSMISSION BY SOIL<sup>1</sup>

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It is the purpose of this paper to describe an improved method for mounting and using porous plates for measuring the relation between soil moisture tension and the moisture content of soils. This apparatus is particularly adapted for making moisture-retention determinations on large numbers of samples. It can be used also for measuring the permeability of soils at moisture contents below saturation.

Compressed air is commonly available, and air pressure is somewhat easier to control above atmospheric pressure than below atmospheric pressure. For this reason the porous plates here described are arranged for installation in a conventional domestic pressure cooker so that various soil moisture equilibria in the 1 atmosphere range can be attained by application of air pressure to a chamber containing the plates. The porous plate mounting, however, is equally suitable for connection to vacuum pressure to accomplish the soil moisture extraction if this arrangement is preferred.

Figure 1 shows the details of construction. The part numbers in the figure correspond to those in the accompanying list. A complete porous plate assembly is shown at *A* in the figure. The method of mounting the porous plate in a copper pan is shown at *D*, and the outlet connection from the under side of the porous plate out through the wall of the pressure cooker to atmospheric pressure is shown at *E*. Provision is made in the present design for mounting four porous plates 11½ inches in diameter in the pressure cooker, and space is provided for soil samples 2.5 cm. high.

The procedure for using the apparatus is as follows: The knurled spouts, part 12, are removed and the plate assembly shown at *A* is set out on to the laboratory bench. The soil samples are usually contained in metal rings from 1 to 2½ centimeters high and may be closely spaced on the porous plate. Free water is maintained on the plate surface until the soils are thoroughly wetted. The plate assembly with soil is then transferred to the pressure cooker. The connection nut, part 5, is engaged in the hole in the cooker wall, and the closure is completed by screwing in the spout, part 12.

A plate frame ring, part 1, is provided for convenience in handling the porous plates. Four lugs, part 2, attached to the ring serve as legs and at the same time make it possible to stack assemblies one on top of another. The align-

<sup>1</sup> Contribution from the U. S. Regional Salinity Laboratory, Riverside, California. Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, in cooperation with the eleven Western State and the Territory of Hawaii.

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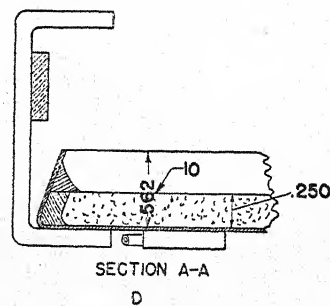


FIG. 1. DRAWING OF PARTS FOR MOUNTING POROUS PLATES IN A PRESSURE COOKER

ment bracket, part 3, and the bronze spring, part 4, hold the frame lugs in register when mounted in the cooker. The inside plate connection nut, part 5, makes connection through the copper tube, part 6, and the attachment button, part 7, to the bottom of the copper pan, part 11. A soft rubber gasket, part 8, which is attached to part 5 with weatherstrip bonding cement makes a convenient seal, as shown in the figure at *E*.

The pans for containing the porous plate are made from 24-gauge sheet copper. The edges can be rolled up with the crimping machine usually available in sheet metal shops. It is not a simple matter to make a trouble-free seal of the porous plate in the copper pan. Though the following method has not been long in use, it is much superior to anything yet tried. After the rolling and forming operations, the bottom of the copper pans should be slightly convex upward. The porous plate is then mounted in place and clamped at about eight points around the periphery with spring clamps.<sup>3</sup> The annular space between the porous plate and the copper pan can then be filled with a water paste of either plastic Portland cement or ceramic tile cement. The latter is preferable, provided the dense impermeable type can be obtained. The clamps can be shifted so as to make a continuous seal. When the cement has set, the clamps can be removed and the excess cement scraped off flush with the porous surface. The plate should be kept wet until the cement is thoroughly hardened, after which the plate is dried and a smooth bead of automobile-top cement is used to make the seal between the porous ceramic plate and the copper pan, as shown in the figure at *D*. This automobile-top cement is commonly available in paste form in collapsible tubes.

<sup>3</sup> The latter can be improvised from ordinary wooden clothespins if the width of bite is increased by placing a short section of  $\frac{1}{4}$ -inch (inside diameter) by  $\frac{1}{8}$ -inch wall Koroseal or rubber tubing over the spring.

Part Num- ber	Num- ber Re- quired	Description	Part Num- ber	Num- ber Re- quired	Description
1	4	Plate frame ring— $\frac{1}{8}$ " x $\frac{1}{2}$ " x 37" brass strip. Roll and silver solder.			value of about $\frac{1}{2}$ atmosphere, mixture No. RA-84, may be obtained from Refractories Division, Norton Co., Worcester, Mass.
2	16	Plate frame lugs— $\frac{1}{8}$ " x $\frac{1}{2}$ " x $3\frac{1}{2}$ " brass strip. Three soldered, one removable on each frame ring.	11	4	Copper pan. Roll from 24-gauge sheet. Use crimping machine.
3	4	Lug alignment bracket— $\frac{1}{16}$ " x $\frac{1}{2}$ " x $1\frac{1}{2}$ " brass strip.	12	4	Outflow spout— $\frac{3}{8}$ " round brass $1\frac{1}{2}$ " long.
4	4	Positioning spring—4" phosphor bronze wire 0.040 diam.	13	1	Base ring— $\frac{1}{4}$ " x $\frac{3}{8}$ " x $11\frac{1}{4}$ " O.D. Roll from strip and silver solder.
5	4	Connection nut $\frac{1}{2}$ " hex brass, $\frac{1}{8}$ ".	14	1	Hose nipple for air inlet. Install opposite to outflow halfway up pot wall.
6	4	Copper tubing—3" long 0.096 O.D.	15	1	Brass cap screw, $\frac{1}{4}$ " x $\frac{1}{2}$ " for anchoring hose nipple.
7	4	Tube attachment button— $\frac{3}{8}$ " brass $\frac{1}{2}$ " long.	16	1	Inlet nipple washer—cut from $\frac{1}{16}$ " sheet rubber.
8	4	Soft rubber gasket. Cut from $\frac{1}{16}$ " sheet stock, 0.500 OD-0.313 I.D. Attach to part 5 with bonding cement.	17	1	16-qt. pressure cooker. National Pressure Cooker Co., Eau Claire, Wisconsin, or equivalent.
9	4	Lug screw—FH brass $\frac{3}{8}$ " x $\frac{1}{2}$ ".	18	1	Petcock $\frac{1}{8}$ " male pipe thread. Screw in pot lid.
10	4	Porous plate—11 $\frac{1}{2}$ " diameter $\frac{1}{4}$ " thick. (Plates with an entry value between 1 and 2 atmospheres may be obtained from Irrigation Engineering Co., Riverside, California. Plates with an entry	19	2	Needle valve. Style No. 396, Hoke, Inc., Englewood, N. J., or equivalent. For use in pressure control system.

It should be of reasonably stiff consistency but should remain somewhat plastic on drying and setting. Two different brands have been used successfully.

The 16-quart pressure cooker used at the laboratory for this purpose may be obtained from the National Pressure Cooker Company, Eau Claire, Wisconsin, or may be purchased locally under various brand names. The inside diameter at the bottom of this cooker is approximately 12 inches and the inside depth of the pot is 8 inches. A suggested detail for the pressure inlet connection to the cooker is given in figure 1C. The petcock, part 18, is installed in the lid of the pressure cooker.

Moisture determinations on a porous plate are ordinarily made on 25- to 30-gm. soil samples, with a sample height of about 1 cm. Such samples can be contained in brass rings 1 cm. high which are cut from  $2\frac{1}{4}$ -inch (outside diameter) by  $\frac{1}{8}$ -inch wall brass tubing. The porous plates here described will accommodate 14 rings of this size.

The apparatus is designed primarily for measuring moisture retention values of soils at discrete tension values in the 1 atmosphere range and is not suitable for obtaining characteristic moisture curves for a given soil sample over a series of tension equilibria obtained by measuring water-outflow increments corresponding to successive air-pressure increments. Deformations in the copper pan which occur with increasing pressure give errors in this case, and pressure-plate apparatus similar to that described by Richards and Fireman<sup>4</sup> should be used for this purpose. The porous plate apparatus described in this paper, however, appears to be quite suitable for measuring the unsaturated permeability of soil columns. In this case, the soil column is mounted in the pressure pot between two of the copper-backed porous plates such as shown in figure 1. The sets of this apparatus which are in use at the Salinity Laboratory were made up in the laboratory instrument shop.<sup>5</sup>

Suggested pressure control systems for use in connection with the apparatus described are indicated in figure 2. The compressed air line at the top of the figure is connected through needle valves (item 19 in list of parts) to the control towers. The water tower shown at A is convenient to use for pressures in the range of 0 to 100 cm. of water. Air leaking past the needle valve slowly builds up pressure in the soil chamber until bubbling starts at the underwater termination of the bubbler tube. The formation of bubbles thus prevents further rise in pressure. It has been found desirable to use tubing of capacity similar to  $\frac{5}{8}$ -inch to  $\frac{3}{4}$ -inch copper tubing, and the bubbler tip can be formed by making a 45° angle cut in the tubing. The type of arrangement shown at A requires no additional manometer for reading the control pressure, provided the 0 for the

<sup>4</sup> Richards, L. A., and Fireman, M. Pressure plate apparatus for measuring moisture sorption and transmission by soils. *Soil Sci.* 56: 395-404, 1943.

<sup>5</sup> This apparatus has been constructed for other laboratories by the Instrument Development and Manufacturing Corporation, Pasadena, California. In mentioning this firm, the Department of Agriculture does not assume any responsibility regarding it, nor does it imply that other manufacturers of instruments are not qualified to perform the same services.



scale is set at the point where the bubbles leave the bubbler tip and the upper level is read for a very low rate of bubbling.

A pressure control water tower using a  $1\frac{1}{4}$ -inch galvanized iron pipe 40 feet high was mounted in a well in a constant-temperature room at the Salinity Laboratory and has given very satisfactory service for a number of years. Wilcox<sup>6</sup> recently described a pressure control system in which the water towers are attached to the outside of the building.

The arrangement shown at figure 2B is substantially the same in principle as that shown at A, except that the greater density of mercury in B makes it pos-

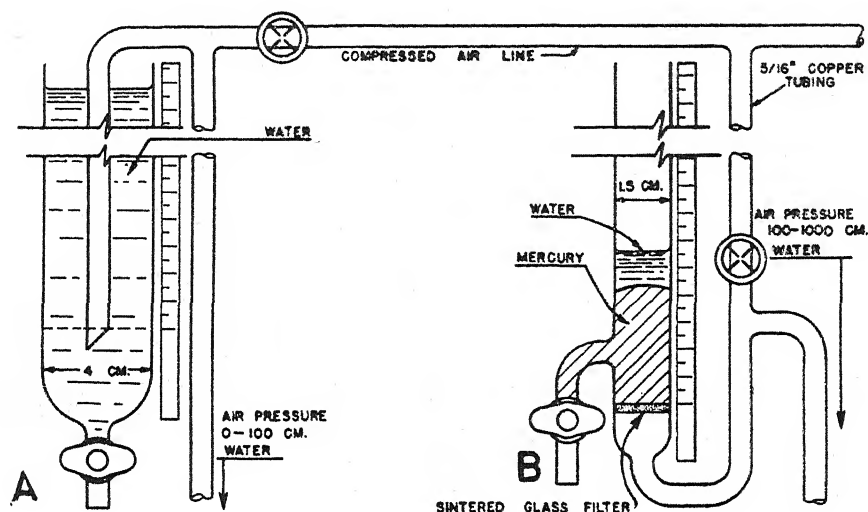


FIG. 2. SYSTEM FOR PRESSURE CONTROL

A—Water tower for pressures from 0-100 cm. of water, B—Mercury tower for pressures from 100-1000 cm. of water. (See text for explanation.)

sible to attain higher control pressures with a convenient length of column. In this case, the mercury is supported on a sintered glass filter, the pores of which are sufficiently fine to support a mercury column of the required height. A fine-porosity Pyrex filter tube in which the porous disc is 1 cm. in diameter seems satisfactory for this use. The mercury column can be  $1\frac{1}{2}$  to 2 cm. in diameter. A smaller diameter does not give sufficient cross section for the air bubbles to rise freely, and a larger diameter requires excessive amounts of mercury. Here again the slow passage of air through the needle valve from the compressed air line causes the air pressure to rise in the soil chamber until the air pressure in the pores of the sintered glass filter exceeds the pressure at the bottom of the mercury column. The formation of air bubbles above the filter surface then prevents a further rise in pressure. It has been found that the upper surface of

<sup>6</sup> Wilcox, L. V. Pressure-control unit for use with the pressure-plate apparatus. In press.

the mercury is maintained in better condition if it is covered by a shallow layer of water. This seems to prevent oxidation and fouling of the mercury, and also prevents the agitation of mercury droplets. It is unnecessary to have a separate manometer to read the control pressure during the operation of this mercury tower. The scale 0 is set at the upper surface of the porous plate, and the control pressure is obtained from the sum of the mercury plus water columns before bubbling is started.

# CLAY MINERAL MODELS: CONSTRUCTION AND IMPLICATIONS<sup>1</sup>

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The study of clays in soils was given great impetus by the recognition of their crystalline nature through x-ray diffraction analysis. Subsequent work has set forth generally accepted atomic structures of the principal groups of clay minerals, although these are still being modified in detail.

Clay mineral structure is basic to soil science. It greatly influences many of the important properties of soils; among these are exchange, release and fixation of ions, and physical structure of soils. In studying the physical and chemical properties of clay minerals as influenced by their atomic structures it is necessary

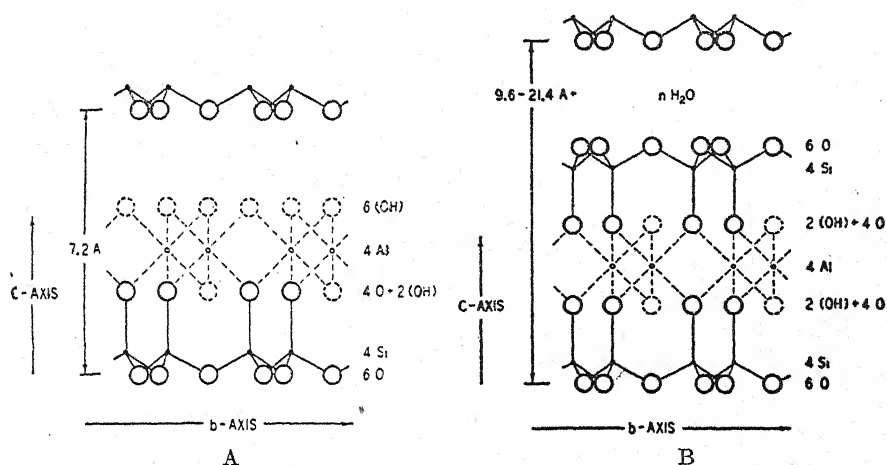


FIG. 1. SCHEMATIC PRESENTATION OF CRYSTAL STRUCTURE OF (A) (LEFT) KAOLINITE AND (B) (RIGHT) MONTMORILLONITE (FROM GRIM)

to make use of visual aids such as diagrams and models. The use of schematic diagrams alone, however, is unsatisfactory, since most of those available do not show the so-called close-packing arrangement of atoms in the structures (fig. 1).

Close-packing models of many organic and inorganic substances have been constructed. Buerger and co-workers (2, 3) have described a technique for the construction of models illustrating the atomic structure of crystals, including silicates. This and similar techniques involve the drilling of holes in wooden or

<sup>1</sup> Journal Paper No. 332, Purdue University Agricultural Experiment Station, Lafayette, Ind. Contribution from the department of agronomy.

<sup>2</sup> Fellows in agronomy and assistant professor of agronomy, respectively. This paper represents equal contributions by each of the authors.

plastic balls at specified angles. The balls are then built into the appropriate structure by connecting them with brass or wooden pins.

The foregoing procedures require special equipment for accurately measuring and drilling holes at the proper angles. This task is both time-consuming and tedious. This difficulty has been overcome in part by the construction of spherical templates (9). The difficulty of constructing the templates, however, limits their practicability. The models thus constructed are rigid and rather fragile. The wooden balls are produced by few firms and are therefore difficult to obtain. It is not practical for students to construct the models themselves because of the time and expense involved.

Hendricks<sup>3</sup> has developed an improvement over previous models by constructing models of strips of plastic material, thereby showing internal structure. These models, however, are rather fragile and require special equipment to make. Hauser (4) has described a method for constructing crystal models by covering cork balls with rubber latex. This method is especially applicable where rigidity of structure is not required.

In seeking a suitable method for constructing models of clay minerals it was found that rubber balls connected by wires adequately served the purpose. The clay mineral structures are composed in large part of oxygens and hydroxyls, and since these have the same atomic radii, only balls of one size need be used in large quantities. Marbles or beads of the proper size may be used to represent the smaller ions such as silicon, aluminum, and magnesium.

#### CONSTRUCTION OF THE MODELS

The materials required for construction of these clay mineral models are small sponge rubber balls approximately 36 mm. in diameter (found in most variety stores), glass marbles approximately 17 mm. in diameter, beads approximately 8 mm. in diameter, soft iron wire, straight pins, and white, green, and black paint.

In figures 2 to 12, oxygen, hydroxyl, and potassium are represented by gray, white, and black balls, respectively; cations in tetrahedral coordination are represented by white beads, and cations in octahedral coordination are represented by black marbles. The numbers of atoms required for constructing the various models are shown in table 1.

The construction of models follows a general pattern of threading rubber balls together with wire in a single plane. Note (figs. 2, 5) the perfect hexagonal symmetry formed by straight lines of oxygens and hydroxyls with the wires intersecting each other at 30 and 60° angles. The positive ions are then placed in their proper position on the negative layers.

The term "sheet" as used in this paper has reference to a single plane of oxygens or of oxygens and hydroxyls. One or more coordinated "sheets" are referred to as a "layer."

The lower sheet of the tetrahedral layer (fig. 2) is constructed by threading the

<sup>3</sup> Personal communication.

oxygen atoms close together as shown; at the center of each group of three atoms a white bead is pinned into position representing the positive ion in tetrahedral coordination (e.g.,  $\text{Si}^{+4}$ ). If an oxygen atom is then placed over each silicon atom, a complete tetrahedral layer is represented (fig. 3). Notice the space between the oxygens in the second sheet; this sheet does not exhibit the close-packing con-

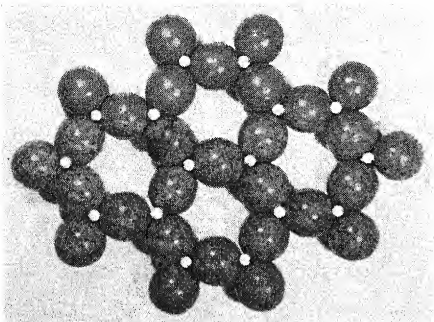


FIG. 2

FIG. 2. LOWER "SHEET" OF TETRAHEDRAL "LAYER"

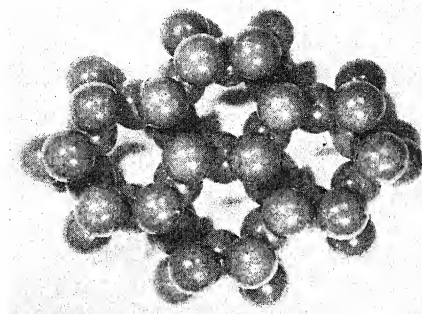


FIG. 3

In this figure and in figures 3 through 12, gray balls represent oxygen atoms; white balls, hydroxyl groups; small white spheres, silicon atoms; black balls, potassium atoms; and small black spheres, aluminum atoms.

FIG. 3. COMPLETE TETRAHEDRAL "LAYER"

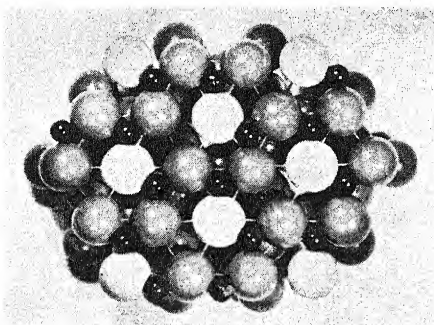


FIG. 4

FIG. 4. TETRAHEDRAL "LAYER" WITH HYDROXYLS AND ALUMINUM ATOMS ADDED

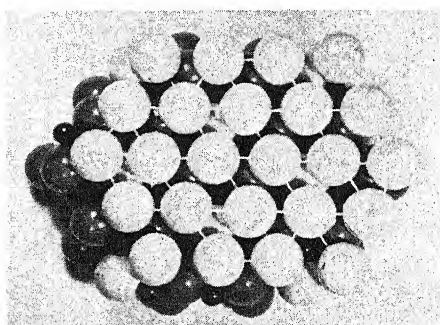


FIG. 5

FIG. 5. VIEW OF KAOLINITE STRUCTURE NORMAL TO THE C-AXIS

figuration characteristic of the first sheet of oxygens. A hydroxyl placed in each vacant space shown in the top sheet of the silica layer (fig. 3), completes the second sheet of negative ions. The trivalent octahedral positive ions (e.g.,  $\text{Al}^{+3}$ ) are now placed in two out of three possible positions as shown in figure 4. The bivalent octahedral positive ions (e.g.,  $\text{Mg}^{+2}$ ) are placed in all three of the possible positions. A third sheet consisting of hydroxyls is placed over the second sheet in a position such that six negative ions surround each positive octahedral ion;



this completes the kaolinite structure represented in figures 5 and 6. Note that the second sheet is common to both tetrahedral and octahedral layers.

The lower two sheets of kaolinite (1:1 type clay mineral) are common to the montmorillonite group (2:1 type clay mineral). The third sheet (fig. 7) and the fourth sheet (fig. 8) of the montmorillonite group are the mirror images of the second sheet (fig. 4) and the first sheet (fig. 2). In montmorillonite the second

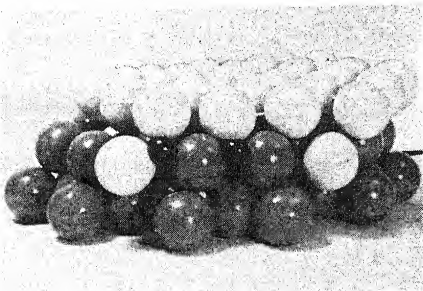


FIG. 6

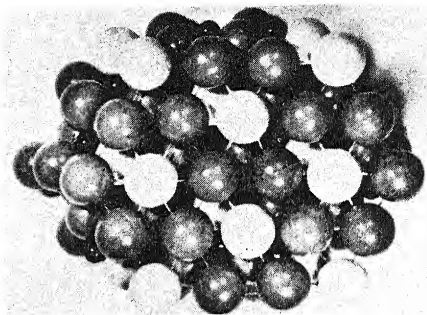


FIG. 7

FIG. 6. VIEW OF KAOLINITE STRUCTURE NORMAL TO THE A-AXIS

FIG. 7. LOWER THREE SHEETS (TETRAHEDRAL LAYER PLUS THIRD "SHEET") OF THE MONTMORILLONITE STRUCTURE

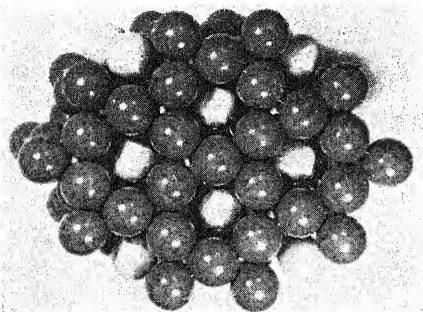


FIG. 8

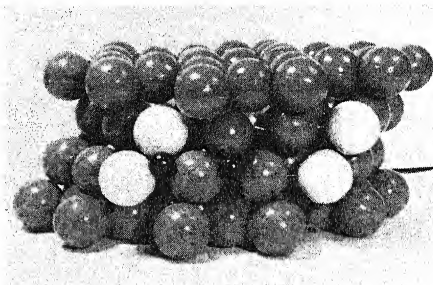


FIG. 9

FIG. 8. VIEW OF MONTMORILLONITE STRUCTURE NORMAL TO THE C-AXIS

The hydroxyl groups, represented by white balls, are actually in the "sheet" below the top "sheet" of oxygen atoms.

FIG. 9. VIEW OF MONTMORILLONITE STRUCTURE NORMAL TO THE A-AXIS

and third sheets of negative ions are common to both the octahedral and the tetrahedral layers (fig. 9).

The mica type mineral is represented by the placement of potassium ions in the vacancies of the silica layer (figs. 10, 11) of the montmorillonite arrangement.

One of the most important features of this procedure for constructing models is the versatility of the structural units. The sheets can be used interchangeably to construct several groups of clay minerals. For example, with five sheets of

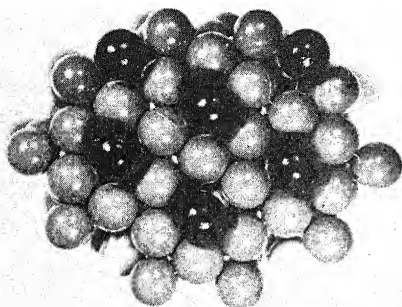


FIG. 10

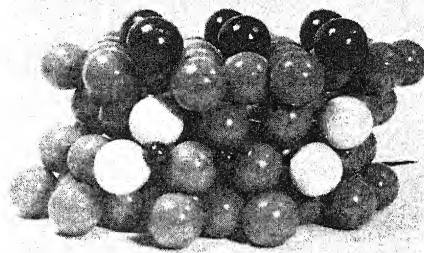


FIG. 11

FIG. 10. VIEW OF MUSCOVITE STRUCTURE NORMAL TO THE C-AXIS

FIG. 11. VIEW OF ONE-HALF THE UNIT CELL OF THE MUSCOVITE STRUCTURE NORMAL TO THE A-AXIS

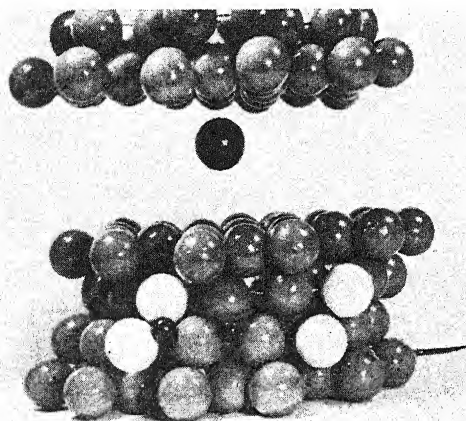


FIG. 12. EXPANDING LATTICE OF MONTMORILLONITE STRUCTURE

TABLE 1

*Number of atoms required in construction of models*

MODEL	NUMBER OF ATOMS			TETRAHEDRAL COORDINATION	OCTAHEDRAL COORDINATION
	Oxygen	Hydroxyl	Potassium		
Kaolinite (figs. 5, 6).....	45	32	..	16	15
Montmorillonite (figs. 8, 9).....	90	16	..	32	15
Montmorillonite (fig. 12).....	180	32	1	64	30
Muscovite (figs. 10, 11).....	90	16	6	32	15

atoms and colored marbles or beads to represent cations, it is possible to represent the typical minerals in the kaolinite, montmorillonite, and mica groups. The sheets may be separated to show internal structure. Variation within the clay

mineral groups can be easily shown in most cases. Isomorphous substitution is conveniently shown by changing the color of the sphere representing the cation. Thus, difference between groups, within groups, and isomorphous substitution can be represented advantageously.

#### IMPLICATIONS

Since conclusions concerning nutrient release and fixation mechanisms in soils are often drawn on the basis of clay mineral structure, it is important to consider the implication of certain clay mineral structure concepts. The following concepts are not usually considered but are suggested by examination of clay mineral models:

1. So-called "close packing"
2. Number of sheets and layers involved
3. Actual size of atoms in the mineral.

The so-called "close packing" of the oxygen atoms is close packing along the c-axis only. The lower sheet of the tetrahedral layer is close packed only in the sense that each oxygen is in contact with four other oxygens, forming a complete hexagonal network (fig. 2). The other two sheets making up the kaolinite type mineral and the two center sheets of the four in the mica type mineral are not close packed, that is, the oxygens or hydroxyls are not in contact (figs. 5, 7).

The second concept refers to the commonly used terms "1:1 lattice type" and "2:1 lattice type." This refers to the number of octahedral and tetrahedral layers, respectively. It is important to note that the 1:1 type lattice actually consists of three sheets of oxygens or hydroxyls (fig. 6) and the 2:1 type lattice actually consists of four sheets of oxygens or hydroxyls (fig. 9).

The third concept probably has the most bearing on studies of the mechanism of fixation. In constructing clay mineral models the relative size of the ions as reported by Landé (5) and Pauling (8) cannot be used. Attempts to build models to scale (using values from tables of ionic radii) showed that the cations may not be the correct size to fit into the compact structures. For example, considering the radii for oxygen as 1.40 Å. and silicon 0.41 Å. (8), the silicon atom would be too large to fit into the center of a compact tetrahedron made up of four oxygens. This implies that either the force field representing atomic size is not spherical or that the ion involved does not have the same size in the clay mineral as it had in the compound in which its size was determined. The latter conclusion is not unreasonable, since the so-called size of an atom is affected by many factors, among which are the nature of the complementary ion, the type of valency, and in general the nature of the environment in which it exists. For example, an aluminum ion in the so-called tetrahedral layer does not have the same size when it is present in the octahedral layer. Pauling (8) has pointed out that the Al-O distance in many octahedral layers is close to 1.90 Å.; in many tetrahedral layers the Al-O distance is in the neighborhood of 1.66–1.76 Å.

Bragg (1) has shown that the smallest diameter of the hexagonal holes in the silica sheet (fig. 3) is 2.6 Å. Page (7) has suggested that potassium ions are

fixed in these holes in the phenomenon of potassium fixation, the commonly considered diameter of the potassium ion being 2.66 Å. Martin *et al.* (6) have shown that rubidium can also be fixed by clays; yet the rubidium ion has a diameter of 2.96 Å. as reported by Pauling (8). This would suggest that these ions could fit only partially into these holes.<sup>4</sup> Page (7) has indicated that this may occur. Since this comparison is based on independently determined cationic sizes and anion-to-anion distances, the comparison may not be valid. *The hole that is 2.6 Å. in diameter with respect to the oxygen atom may not be the same size with respect to potassium or any other ion.* In general, the smaller the unoccupied space or pore, the greater the percentage uncertainty as to its exact size.

The difference in the size of an ion in different compounds is a danger signal to the investigator who attempts to determine spacings by adding up ionic sizes.

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<sup>4</sup> It would be revealing to know whether cesium, diameter 3.38 Å., also exhibited this phenomenon of fixation.





# CHEMICAL AND PHYSICAL BEHAVIOR OF COPPER IN ORGANIC SOILS<sup>1</sup>

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Practical recommendations regarding the use of a given plant nutrient in the fertilization of a crop can be used to much greater advantage if something is known of the physical and chemical behavior of the element in the soil involved. Of major nutrients, such as phosphorus and potassium, the amount applied to soils of low fertility is governed to some degree by the amount consumed by the crop. Of some of the minor elements, however, the amount consumed by the crop is only a very small fraction of that normally applied to the soil for correcting plant deficiencies. For this reason an understanding of the behavior of minor elements in soils is especially important. In this paper an attempt is made to answer some of the questions about the chemical behavior of copper in organic soil.

## REVIEW OF LITERATURE

Reactions involving applied copper and which occur in the soil itself have been but little investigated. Jamison (6) reported that the particle size of copper sulfate affected its solubility in Norfolk sand.

Allison (1) reported that a considerable portion of the copper cation applied to organic soils was held rather tenaciously in the top few inches of the soil. Skaptason (10) accounted for an increase of 180 pounds of copper per acre in the top 6 inches of Long Island soils, when approximately 20 pounds of copper per year for 32 years had been applied in the form of bordeaux sprays.

Most workers report that copper availability decreases with increased alkalinity of the soil. Piper (8) found that an increase in acidity for any given level of copper increased the availability somewhat when measured either chemically or by total copper absorbed by plants. Peech (7) reported similar data. Teakle *et al.* (12) reported plants were acutely deficient in copper when grown on marly soils of Western Australia. Teakle (13) also reported that applications of 2 to 10 pounds of copper sulfate per acre to these soils were sufficient to correct a copper deficiency. The residual values of such small applications of copper were so substantial that the succeeding crops showed little or no response to additional applications.

The soil in areas where copper deficiency in plants have been reported is not necessarily alkaline. Harmer (5) observed that, in general, the more acid the organic soil, the greater was the relative response to copper, and the greater the number of crops that were likely to respond to the copper application. Teakle and Stewart (11) were able to show spectacular benefits from application of copper to a very acid muck (pH 4.2).

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<sup>1</sup> Part of a thesis presented by the author in partial fulfillment of the requirements for the degree of doctor of philosophy, published with the approval of the Graduate Council and the director of the Michigan Agricultural Experiment Station, East Lansing, as Journal Article No. 927 (N.S.). The author was formerly graduate fellow, soil science department, Michigan State College, and is now agronomist at the William Gehring Farms, Rensselaer, Indiana. He expresses his appreciation to Paul M. Harmer, soil science department, for his guidance during the progress of this work, and to E. J. Benne, agricultural chemistry department, Michigan State College, for his suggestions and helpful criticism.

Bower and Truog (3) found that the base-exchange capacity of a soil, as shown by use of copper acetate, was nearly twice as high as values obtained by use of monovalent cations. For example, two soils with exchange-capacity values of 117 and 60 m.e., as determined by standard methods, had values of 230 and 115 m.e., respectively, when exchange capacity was determined by use of copper acetate. These workers believed that the exchange adsorption was  $(\text{HO-Cu})_{2x}$ -clay instead of  $\text{Cu}_x$ -clay.

Probably the best work so far reported on the cation-exchange reactions of zinc is that of Elgabaly and Jenny (4). Since the chemical reactions of zinc are similar to those of copper, probably many of the findings would apply to reactions of copper in the soil. These investigators found that the addition of zinc chloride to either a sodium or a calcium bentonite (clay) released less sodium or calcium than the total milliequivalents of zinc adsorbed. In other words, the reaction is not stoichiometric. It was also noted that the adsorption of zinc involved an adsorption of chloride anions. Additions of zinc chloride to a calcium bentonite produced a complex colloidal system of adsorbed cations containing  $\text{Ca}^{++}$ ,  $\text{Zn}^{++}$ ,  $(\text{ZnCl})^+$ , and  $(\text{ZnOH})^+$ .

Wood (14) believed that the copper extracted by boiling normal nitric acid represents that which, through weathering and other processes, may become available for plant use as the exchangeable supply is lowered. The amount of copper leached by ammonium acetate from a 5-gm. soil sample was less than 1. p.p.m.

#### EXPERIMENTAL PROCEDURE

The laboratory studies were made with organic soil samples obtained from the Michigan State College Muck Experimental Farm. Ten to twelve borings with an auger type sampler were collected from each plot (three replications per treatment) on the minor element series. Borings from each treatment were combined, thoroughly mixed, and stored in a moist condition in glass bottles. Chemical properties of the soil were determined on moist samples, but the chemical values were expressed on the basis of soil dried at 90° C.

The carbamate method (2) was used for determination of micro-concentrations of copper, and the final readings were made with an Evelyn photoelectric colorimeter. In the study of adsorption of the element at various symmetry values, the copper in solution was measured as the cupra-ammonia complex by adding 20 ml. of dilute ammonia to 5 ml. of copper solution (9). For the latter determination a 6,200-A. filter was used.

In the study of adsorption of copper at various pH levels, samples of moist soil equivalent to 7.1 gm. of dry soil were leached with 0.2 N HCl in a Büchner funnel until the pH of the soil was approximately 3.0. The soil was then leached with water, and the pH of the soil adjusted to the desired value with lime water. The soil was next dispersed in 100 ml. of water containing 2.0 mgm. of copper sulfate. After intermittent stirring for several hours, the solution was again filtered, and copper not adsorbed was measured. A similar procedure was followed in which the soil sample was treated with 100 ml. of 0.5 N copper sulfate. The larger application of copper sulfate produced considerable acidity, for the pH value of the suspension was around 3.3. The suspension was adjusted to the original pH with concentrated sodium hydroxide. For these soils the copper sorbed, rather than that not sorbed, was measured. Measurement was made by leaching excess copper from the soil with 300 ml. of  $\text{CO}_2$ -free distilled water and then leaching with 500 ml. of 0.2 N HCl to remove adsorbed copper. Copper was measured colorimetrically as the cupra-ammonia complex.

In the preparation of a Cu-muck, the soil was first leached with dilute hydrochloric acid to remove all the bases. This operation was followed by leaching, first with water and finally with 200 ml. of 0.5 *N* copper solution. Excess copper was leached out with 400 ml. of cold water. Total adsorbed copper was measured as described previously.

In the study of the chemical reaction of Cu-muck with sodium hydroxide or hydrochloric acid, a Fisher titrimeter was used to measure the electrical resistance (ohms). Readings were made 1 minute after addition of the base or acid. The reciprocal of ohms (conductivity) was used in plotting the curve.

In the preparation of 0.5 *N* copper acetate solution, 2 ml. of concentrated acetic acid were added per liter to dissolve all traces of copper hydroxides. The pH of the resultant solution was 5.3.

#### RESULTS AND DISCUSSION

Of prime consideration in a study of most plant nutrients in soil is determination of the relationship between total and available nutrients. In table 1 are shown the data for the total copper content of soil sampled from the minor element plots at the Michigan Muck Experimental Farm. It is quite evident that the soil analyses of the 0-8-inch depth correlate with the different treatments. The copper content of soil sampled from plot 3 was nearly treble that of soil from the control plot. Analysis of the 24-30-inch soil depth indicates only slight accumulation of copper in the lower horizons. Since virtually all the copper applied to the soil was in the 0-8-inch depth, it can be concluded that leaching was not a great factor in the organic soil studied in this investigation. The figures in the last column illustrate this fact. If the 0-8-inch depth is assumed to weigh 500,000 pounds of oven-dry soil—a figure substantially correct by actual measurement—the copper sulfate equivalent in plot 3 was 76 pounds. The difference between the amount in plot 1 and plot 3 is 48 pounds, which accounts for virtually all the original application of 50 pounds, even though it had been applied 5 years before soil sampling. Similar comparison of plot 2 showed that a total of 232 pounds of the original 300-pound application was still in the topsoil. Plot 4 showed that approximately 212 pounds remained from the total application of 250 pounds.

Attempts were made to differentiate between available and total copper from soil sampled from the minor element plots. Table 2 shows some of these results. Wood (14) suggested the use of boiling *N* HNO<sub>3</sub> for extracting from the soil the copper considered available for plants. This procedure was not suitable for organic soils because of the extreme frothing. As shown in table 2, leaching the soil with 400 ml. of cold nitric acid extracted a major portion of the total copper. The copper utilized yearly by crops grown on the control treatment generally amounts to less than 0.03 pound per acre. The copper extracted by nitric acid from plot 1 was equivalent to 4 pounds per acre. This amount is more than 100 times as great as that consumed annually by plants, which shows that the method does not measure readily available copper. When hydrochloric acid was used instead of nitric acid, about the same amount was extracted. It would

appear from these results that the use of cold strong acids for digesting muck soils extracted total rather than readily available copper.

Leaching the soil with 400 ml. of neutral normal ammonium acetate indicated no copper removal, as the copper impurities in the blank solution were greater than the leachings from the soil. The same ammonium acetate, with the pH adjusted to 4.5 by concentrated acetic acid, likewise failed to extract any appreciable amounts of copper.

TABLE 1  
*Fixation of copper in an organic soil (pH 6.1)*

TREATMENT*	TOTAL COPPER CONTENT		CuSO <sub>4</sub> EQUIVALENT IN TOPSOIL†
	Top 0-8 inches	Subsoil 24-30 inches	
	p.p.m.	p.p.m.	lbs./A.
Plot 1—control.....	14	8	28
Plot 3—50 lbs. CuSO <sub>4</sub> per acre in 1942 only.	38	9	76
Plot 2—300 lbs. CuSO <sub>4</sub> per acre in 1942 only...	130	13	260
Plot 4—50 lbs. CuSO <sub>4</sub> per acre annually 1942 through 1946.....	120	10	240

\* Samples collected in the fall of 1946 from minor element series of the Michigan Muck Experimental Farm.

† Calculated on a basis of 500,000 lbs. of oven-dried soil per acre.

TABLE 2  
*Copper extracted by nitric acid and ammonium acetate from organic soil*

PLOT NUMBER*	COPPER		
	Total in soil	Extracted with N HNO <sub>3</sub>	Extracted with N NH <sub>4</sub> AcO
	p.p.m.	p.p.m.	p.p.m.
1	14	8	0
3	38	29	0
2	130	104	0
4	120	92	0

\* For treatment see table 1.

It can be concluded from the results shown in table 2 that copper in slightly acid soil does not exist in the exchange complex. When copper as copper sulfate is added to the soil under field conditions, it probably changes to the oxide and hydroxide forms. When combined as an oxide, copper is easily dissolved by strong acids.

To determine the reactions of copper sulfate under laboratory conditions, 20 gm. of moist soil (7.1 gm. dried at 90° C.) was suspended in 100 ml. of water containing copper sulfate. Table 3 shows the amounts of copper in solution 3 hours after preparation of the suspension. When the copper was added at levels equivalent to 10, 100, and 1,000 p.p.m., by dry soil weight, the amounts of copper

not sorbed were 2.9, 0.9, and 0.4 per cent, respectively. After removal of the copper not sorbed, the soil was leached with 400 ml. of neutral normal ammonium acetate solution. The results show that increasing the amount of copper sulfate increased the water-soluble and exchangeable copper but decreased the percentage recovery.

TABLE 3  
*Sorption of copper by organic soil (pH 6.1)*

COPPER APPLIED	COPPER NOT SORBED		Cu EXTRACTED BY 400 ML. NEUTRAL $\text{NH}_4\text{AcO}$	
	Total	Recovery	Total	Recovery
	mgm.	per cent	mgm.	per cent
Control* . . . . .	0	...	0	...
0.07 mgm. (10 p.p.m.) . . . . .	0.002	2.9	0.003	4.3
0.07 mgm. (100 p.p.m.) . . . . .	0.006	0.9	0.022	3.1
7.0 mgm. (1,000 p.p.m.) . . . . .	0.030	0.4	0.206	2.9

\* Soil contained about 0.1 mgm. of copper.

TABLE 4  
*Sorption of copper by 20 gm. of moist soil at various pH levels*  
Exchange capacity of sample, 8.9 m.e.

pH	COPPER NOT SORBED ON ADDITION OF 2.0 MGm. $\text{CuSO}_4$	COPPER SORBED FROM 100 ML. 0.5 N $\text{CuSO}_4$
	mgm.	m.e.
3.0	0.012	5.3
3.3	0.011	6.3
3.7	0.011	6.6
4.0	0.011	7.3
4.3	0.009	7.5
4.7	0.009	10.6
5.0	0.008	*
5.3	0.008	*
5.8	0.006	*
6.1	0.006	*
6.4	0.007	*
7.2	0.006	*

\*  $\text{Cu}(\text{OH})_2$  precipitated.

When it became evident that pH affects the reaction of copper in the soil, two experiments were set up: one consisted of soil samples treated with 2.0 mgm. of copper sulfate; the other, of soil treated with excess copper sulfate, which amounted to 100 ml. of 0.5 N  $\text{CuSO}_4$ . The data are shown in table 4. The amount of copper not sorbed (water-soluble) doubled with a change in soil pH from 5.8 to 3.0. The results are in agreement with the statement that copper solubility increases with increase in soil acidity. The soil that received excess copper sulfate showed low adsorption at extremely acid levels. Attempts to



adjust the pH of the suspension above 4.7 obviously showed that all the copper hydroxide precipitated before the adjustment point could be reached.

The high amount of copper sorption at pH 4.7 indicates that possibly some copper hydroxide was precipitated at this point. The reactions of copper in soils more acid than pH 4.7 are with the exchangeable complex. In soils less acid than 4.7, some of the copper probably would be precipitated as the hydroxide; the remainder would be involved in other exchange reactions.

The relative ease of adsorption of copper and hydrogen, was studied with two systems of muck: a H-muck, obtained by leaching the muck with hydrochloric acid and then washing out the excess acid; and a Cu-muck, derived from a H-muck and prepared both from copper sulfate and from copper acetate. The Cu-muck was prepared by slowly leaching the H-muck with 300-400 ml. of

TABLE 5  
*Replacement of copper from Cu-muck with different concentrations of hydrochloric acid in a soil-water suspension*  
Exchange capacity of samples, 8.9 m.e.

HCl ADDED	SOIL SATURATED WITH $\text{CuSO}_4$ -pH 3.2			SOIL SATURATED WITH $\text{Cu}(\text{AcO})_2$ -pH 5.3		
	$\text{Cu}^{++}$ Replaced	Total copper sorbed	Percentage copper replaced	$\text{Cu}^{++}$ replaced	Total copper sorbed	Percentage copper replaced
<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>		<i>m.e.</i>	<i>m.e.</i>	
2.5	1.80	5.74	31	2.66	13.0	20
5.0	2.61	5.65	46	5.04	13.7	37
7.5	3.76	6.08	62	7.30	14.2	51
10.0	4.33	6.40	68	8.84	13.2	67
20.0	4.71	5.78	81	11.20	14.1	79
40.0	5.42	6.22	87	11.20	12.6	89
Average .....		6.0	..	.....	13.5	..

0.5 N copper solution and then leaching out the excess copper with  $\text{CO}_2$ -free distilled water. The use of alcohol was not found to be satisfactory because of the precipitation of some of the copper in solution. To investigate equilibrium reactions, a given weight of soil was suspended in water and brought up to a volume of 200 ml., after the addition of either the acid or the copper salt. The suspension, after standing several hours with occasional stirring, was filtered. The adsorbed copper was measured by leaching the soil with excess 0.2 N HCl.

Table 5 shows the values for displaced copper after equilibrium had been established between the soil and a definite amount of hydrochloric acid. Since the exchange capacity of the soil is 8.9 m.e., the equilibrium reaction on addition of 10.0 m.e. of hydrogen is the value at 1.1 symmetry. The percentage replacement of copper by hydrogen was similar whether Cu-muck was derived from copper sulfate or from copper acetate, even though the total amount replaced was considerably different. There appeared to be little difference for either salt at the different concentration levels. Since HCl equal to 1.1 times the symmetry

value released approximately two thirds of the total sorbed copper, the ratio of copper to hydrogen in the solution was 2 to 1.

Approximately 89 per cent of the copper was replaced from the muck soil on addition of 40 m.e. of hydrochloric acid, which suggests that hydrogen can effectively replace adsorbed copper. An interesting difference in the two copper salts is shown in table 5. The total copper adsorbed by soil from copper sulfate amounted to about 6.0 m.e., whereas the value for copper acetate averaged 13.5 m.e. Since 6.0 m.e. is less than the exchange capacity of 8.9 m.e., it is possible that most of the copper sorbed was in the divalent form. The large amount of exchangeable hydrogen was caused by the strongly acidic properties of copper sulfate. The chemical behavior of copper acetate is quite different from that of copper sulfate, in that the total copper sorbed is greater than the exchange capacity of the soil. With the method used, the value for copper sorbed was not double the original exchange-capacity figure, however, as Bower and Truog (3) were able to show. Each adsorbed copper cation is not neutralizing two charges

TABLE 6  
*Replacement of hydrogen from H-muck by addition of varying amounts of cupric ions*

Cu <sup>++</sup> ADDED	COPPER SORBED FROM ADDED CuSO <sub>4</sub>		COPPER SORBED FROM ADDED Cu(AcO) <sub>2</sub>	
	m.e.	per cent	m.e.	per cent
2.5	1.87	75	2.48	99
5.0	2.44	49	4.75	95
7.5	2.67	36	6.82	91
10.0	3.08	31	9.04	90
20.0	3.64	18	10.6	53
40.0	4.59	11	11.1	28

on the colloid, but is acting as a complex cation with an acetate or hydroxyl anion neutralizing one of the two copper valences.

Table 6 shows the amounts of copper sorbed by H-muck on addition of copper sulfate or copper acetate to the suspension. The values for copper sulfate agree closely with those in table 5. For example, 31 per cent of the copper was sorbed by the soil on addition of 10.0 m.e. of copper, or 69 per cent was in solution in comparison with the 68 per cent shown in table 5. With the addition of copper acetate to the acid muck, entirely different values were obtained. At approximately 1 symmetry (10 m.e.) 90 per cent of the copper was sorbed. Additions higher than 1 symmetry naturally had low percentage sorption values because the soil was nearly saturated with copper. This behavior of copper acetate made possible its use for measuring the exchange capacity of soils (9). The formation of acetic acid, which has a low dissociation value, permitted the copper to replace a greater proportion of hydrogen on the muck soil than was possible with copper sulfate, which formed some sulfuric acid.

The same soil reported on in tables 4, 5, and 6 was used to study further the reactions of copper as determined by conductivity methods. It was believed that this method could help in differentiating the various proportions and types

of adsorbed copper on the colloid. Determination of adsorbed ammonium by the standard ammonium acetate method (2) showed that the exchange capacity of the soil sample was 8.9 m.e. The exchange capacity as determined by the titrimetric method indicated that the value was 10.5 m.e. when H-muck was titrated with 0.48 N NaOH. The difference in values obtained by the two methods made it difficult to decide which method was preferable for evaluating exchange capacity. The value of 8.9 was used for interpreting figures 1 and 2.

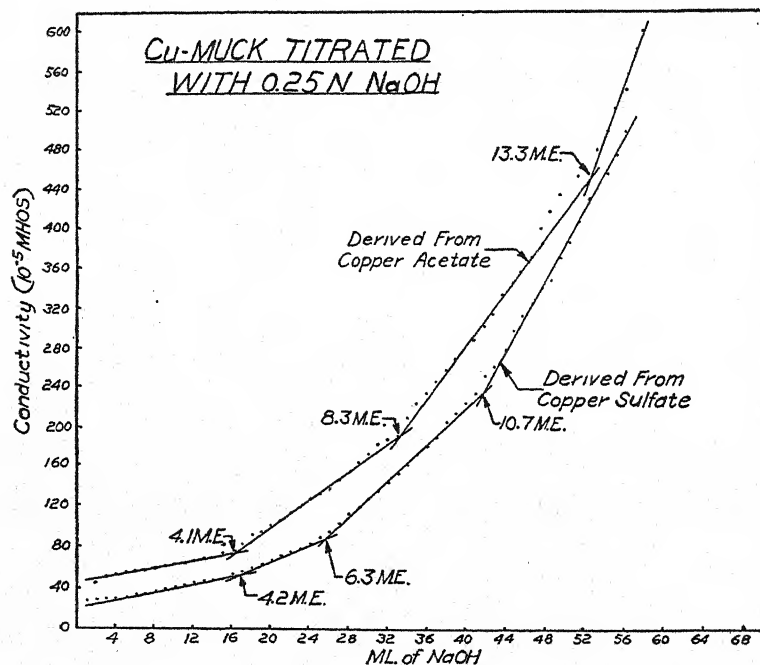


FIG. 1. CONDUCTIVITY MEASUREMENTS OF Cu-MUCK WHEN TITRATED WITH NaOH

The principle upon which a titrimetric measurement is based is that, as each colloidal system becomes saturated with a different cation, a change in the electrical conductivity of the suspension occurs. The curves in figure 1 illustrate the fact that Cu-muck is a complex system. They are the results of titrating with NaOH, a Cu-muck derived from a H-muck either by leaching with an excess of 0.5 N copper sulfate or with copperacetate. The dots on the figure are actual measurements. The straight lines are lines considered to fit the curve best. At each intersection of the lines the milliequivalent value is shown.

Any interpretation of figures 1 and 2 must agree with other known facts. For example, in table 5, the data showed that the total copper sorbed by the soil, when derived from  $\text{CuSO}_4$  and  $\text{Cu}(\text{AcO})_2$ , was 6.0 and 13.5 m.e., respectively. The curve for copper acetate in figure 1 shows that the final equivalent point is 13.3, which is similar to the total milliequivalents of adsorbed copper. If the copper is adsorbed as  $\text{Cu}(\text{OH})^+$ , which was suggested by Bower and Truog (3),

no reasonable explanation could account for all these "breaks in the curve, nor could the total milliequivalents be greater than the exchange capacity of the soil when titrated with NaOH, provided copper hydroxide is assumed to be the end

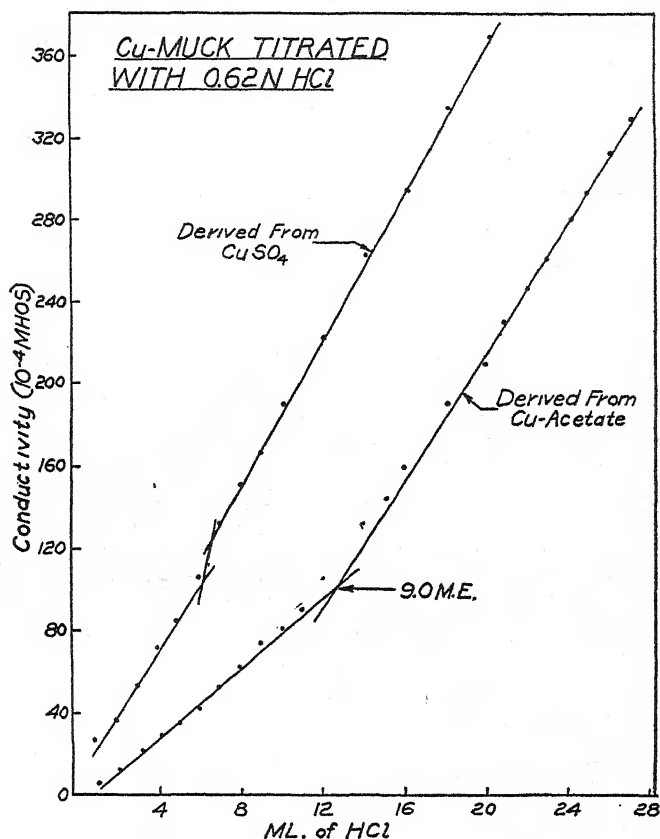
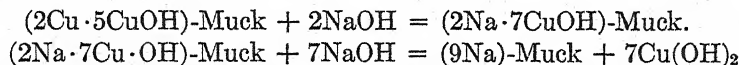


FIG. 2. CONDUCTIVITY MEASUREMENTS OF Cu-MUCK WHEN TITRATED WITH HCl

product. For example, if a soil system had 4 m.e. of  $\text{Cu}^{++}$ , and 5 m.e. of  $\text{Cu}(\text{OH})^+$ , the reactions would be:

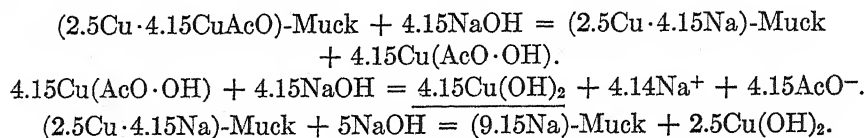


In such a reaction it would take 9 m.e. of  $\text{Na}^+$  to replace 14 m.e. of  $\text{Cu}^{++}$  on the colloid. One then could expect equivalent points at 2.0 and 9.0 m.e. The latter would be identical with the soil-exchange capacity.

The points shown in figure 2 substantiate the belief that copper does not exist as  $\text{Cu}(\text{OH})^+$ . There was only one obvious equivalent point, at 9.0 m.e., a value nearly identical to that of the exchange capacity of the soil. In order to account for the 13.5 m.e. of copper known to be adsorbed, the copper would have to be

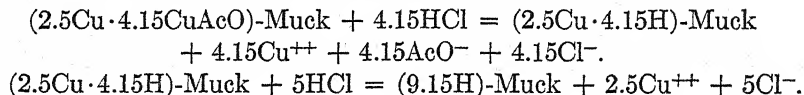
combined with an acidic compound such as  $(\text{CuAcO})^+$  instead of the hydroxyl group.

The curve for the NaOH titration of Cu-muck derived from copper acetate appears to show that a double reaction is taking place, since the point 4.1 is approximately equidistant from 8.3 and 0. The third reaction requires a replacement of 5.0, which is the difference between 13.3 and 8.3. The following series of reactions are proposed to fit these conditions:



It can be observed that 13.3 m.e. of  $\text{Na}^+$  was required to replace and precipitate the adsorbed copper. The exchangeable copper was, likewise, 13.3 m.e. The actual amount of  $\text{Na}^+$  on the colloid amounted to 9.15 m.e. It was first thought that some exchangeable hydrogen was still on the exchange complex. Apparently there is very little hydrogen, for it could not be accounted for on any portion of the curve. The ease of replacement of exchangeable hydrogen by copper acetate, as shown in table 6, would tend to confirm this fact. Furthermore, the hydrogen-ion concentration of water at pH 5.3 amounts to less than 0.01 m.e. per liter.

Using the Cu-muck complex proposed in the sodium hydroxide reaction, we find that there would have to be two reactions when the soil is titrated with hydrochloric acid. The following equations illustrate these reactions:



The primary difference in the reactions with  $\text{H}^+$  and  $\text{Na}^+$  is that copper remains ionized in acid solutions and is precipitated in alkaline solutions. It is also to be noticed that addition of 4.15 m.e. of  $\text{H}^+$  releases 8.3 m.e. of  $\text{Cu}^{++}$ . The total of 9.15 m.e. of  $\text{H}^+$  required for the two reactions is considered to be in good agreement with the 9.0 point shown in figure 2. If there is a break in the curve between the first and second reaction in the acid titration, it could not be detected. This is not surprising, since the conductivity of  $\text{Cu}(\text{AcO} \cdot \text{Cl})$  would be very similar to  $\text{CuCl}_2$ . Both compounds would be highly dissociated in dilute solution.

The reactions for Cu-muck derived from copper sulfate would be different from those for Cu-muck derived from copper acetate in that a considerable amount of hydrogen is adsorbed. The first reaction of NaOH would be to replace any hydrogen. This required 4.2 m.e. The difference between 4.2 and 10.7 represents the exchange and precipitation of  $\text{Cu}^{++}$  and  $(\text{CuSO}_4)^+$ . Titration of the colloid with hydrochloric acid would show only the reactions with the adsorbed copper. Figure 2 shows the curve for this reaction. Because of the peculiarity of the titration curve, no definite intersection could be prescribed for the Cu-muck derived from copper sulfate.



## SUMMARY

In a study of the physical and chemical reactions of copper in organic soil from the Michigan Muck Experimental Farm, the following results were obtained:

Copper, applied as the cupric ion, to organic soils was found to be held rather tenaciously in the zone of placement. Soils collected 5 years after a 50-pound-per-acre application showed that approximately an equivalent of 48 pounds of copper sulfate remained in the upper 8 inches. From an original application of 300 pounds of copper sulfate per acre, 232 pounds were found to be in the topsoil (8-inch layer).

A large portion of the copper in organic soils could be extracted with normal nitric or hydrochloric acid, but very little with ammonium acetate.

Copper sulfate was precipitated, probably as the hydroxide, when the pH of the soil-water suspension was greater than 4.7.

Studies of equilibrium reactions of copper and hydrogen in organic soils showed that the ratio of adsorbed cations at symmetry concentration was approximately two equivalents of hydrogen to one equivalent of copper.

Saturating a H-muck with copper by leaching with copper acetate showed that there was no simple exchange reaction. Titrimetric studies indicated that the copper was adsorbed as the divalent cation  $\text{Cu}^{++}$  and as the monovalent cation complex  $(\text{CuAcO})^+$ .

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# BEHAVIOR OF MANGANESE IN THE SOIL AND THE MANGANESE CYCLE<sup>1</sup>

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Many of the soils in Hawaii which are utilized for agricultural purposes are characterized by a high manganese content. This is particularly marked in the red residual soils which comprise a major portion of Hawaiian soils. Most of these soils have a total manganese content ranging from 1 to 4 per cent. Wilcox and Kelley (31) in their work with manganiferous soils gave analyses ranging from 4.43 to 9.74 per cent  $Mn_2O_3$ . Though admittedly the total analysis of manganese in the soil is not a measure of availability to plants, it is generally accepted that a certain portion of the total is potentially available and may play a role in the nutrition of plants. If it is remembered that a total manganese content of greater than 0.25 per cent is considered high in many sections of the United States, the magnitude of the manganese problem in Hawaii becomes apparent.

Many of the crops grown in Hawaii apparently are not affected by the high manganese content of the soil. Sugarcane, the major agricultural crop, and grasses in general seem to thrive on these soils and are not affected adversely. Growers of pineapple, however, experienced some difficulties with the manganese problem. When pineapples were grown on the highly manganiferous soils, the yields were low and the general appearance of the plants was poor. The earlier investigators believed that the high concentration of manganese in the soil was toxic to pineapples. According to Johnson (10), the problem was not that of direct manganese toxicity, but rather of manganese-induced iron deficiency which brought about a chlorosis of the pineapple plant. No report on the effects of excess manganese on the growth of other crops in Hawaii has been published. Some of the workers at the Hawaii Agricultural Experiment Station have indicated,<sup>3</sup> however, that manganese may be toxic to or may limit the growth of many truck crops. It has also been the experience of the writers that difficulties are encountered in growing legumes and other crops in the manganiferous soils.

Although in Hawaii a number of workers have investigated and analyzed the total and available (acid- and water-soluble) manganese in soils, very little work has been done on means of controlling or influencing the available form. In this study an attempt was made to determine the soil treatments and soil conditions

<sup>1</sup> Contribution from the department of agricultural chemistry and soils of the Hawaii Agricultural Experiment Station, University of Hawaii, Honolulu, T. H. This study includes the work done for the degree of master of science by the senior author, and other work done at this Station. Published by permission of the director as Technical Paper No. 170.

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<sup>3</sup> Personal discussion.

which influence the availability of manganese, with the aim of controlling this condition in the soil.

#### REVIEW OF LITERATURE

Much work has been done on the availability of manganese in soils and on the factors which influence manganese availability. This work can readily be classified under three general headings, as follows:

1. Effect of physical changes.
  - a. Changes in temperature (2, 5, 11, 16, 29).
    1. Heating releases manganese.
    2. Steam-sterilization releases manganese.
  - b. Changes in water saturation (5, 16, 24, 29).
    1. Water-logging releases manganese.
    2. Wetting of soils (but to a lesser degree than that of water-logging) fixes manganese.
    3. Drying releases manganese.
2. Effect of chemical changes.
  - a. Changes in pH (2, 4, 8, 9, 12, 17, 19, 33).
    1. Increase in pH fixes manganese.
    2. Reduction in pH releases manganese.
    3. Addition of acids and acid-residual fertilizers releases manganese.
    4. Addition of alkali and basic-residual fertilizers fixes manganese.
    5. Addition of sulfur releases manganese.
  - b. Changes in oxidation-reduction conditions (24, 28).
    1. Addition of reducing agents (quinone, quinhydrone, sodium sulfite, formaldehyde, starch, sugar, etc.) releases manganese.
  - c. Addition of halides (26).
    1. Addition of iodides releases manganese.
    2. Addition of fluorides fixes manganese.
    3. Addition of bromides fixes manganese in alkaline soils.
    4. Addition of large amounts of chlorides releases manganese.
  - d. Addition of phosphates (1, 27, 33).
    1. Sometimes manganese is fixed and sometimes released (results are conflicting).
3. Effect of biological activity.
  - a. Bacterial activity fixes manganese (6, 7, 14, 18, 20).

#### EXPERIMENTAL PROCEDURE

For the major part of this study, soil from the Poamoho substation of the Hawaii Agricultural Experiment Station was used. This soil was selected because of its high manganese content, which would make changes in the manganese level quite evident. At a later stage in the experimentation, soils from Manoa, Aiea, and Koko Head were used. The Manoa soil, a soil of medium manganese content, was taken from a vegetable crop field at the University of Hawaii. The Aiea soil, which is high in manganese content, was from a sugarcane field. The Koko Head soil, which is medium in manganese content, was from a farm in that section.

The analytical method used in the determination of manganese was essentially the same as the colorimetric method of Willard and Greathouse (32), with modifications by Fujimoto and Sherman (5). The color of the manganese solution was read with a photoelectric colorimeter with a green filter which had a trans-

mission range of 500 to 570  $m\mu$  wave length of light with maximum transmission at 530  $m\mu$ .

To determine the effects of the various soil treatments upon the availability of manganese, the soils were initially treated with various substances, moistened to approximately the moisture content at maximum field capacity, and allowed to stand in the laboratory for 2 weeks. The exchangeable manganese was then extracted with normal ammonium acetate solution adjusted to pH 6.8. In the treatments in which fixation of manganese was expected, the soils were initially oven-dried to increase the exchangeable manganese to a high level, so that any decrease in the level would be of a greater magnitude than would be expected if an unheated soil were used. In the treatments in which release of manganese was expected, unheated soil was used.

During the latter part of the investigation, an effort was made to obtain some evidence of the chemical or physical reactions of manganese in the soil. To do this, the soil was treated with a number of reducing agents, wetted to the moisture content at maximum field capacity, and extracted with ammonium acetate solution. The extracted soil was then oven-dried at 105°C. for 24 hours and reextracted with ammonium acetate solution to see whether the hydration-dehydration hypothesis of Fujimoto and Sherman (5) could be verified or confirmed.

Most of the laboratory chemical treatments were also duplicated in the greenhouse. The soils were given the various treatments and were placed in gallon-sized pots, to each of which was added the equivalent of 500 pounds of fertilizer (7-14-14) per acre. Each treatment had four replicates. Four cowpea plants were grown in each pot. The cowpea was selected because of its rapid growth and relatively simple germination. After a short period of growth, the plants were harvested, dried, and weighed. The dried plant parts were then ground and analyzed for total manganese. The yields are presented, but no attempt to interpret the yield data is made, for the sole purpose of growing the plants was to determine whether there was any correlation between plant absorption of manganese and laboratory findings of release or fixation of manganese in the soil.

The procedure is described here in a rather general way, except where a more detailed description appears necessary.

The following soil treatments were used in this study: liming materials and bases [ $\text{Ca}(\text{OH})_2$ , dolomite,  $\text{NaOH}$ , and  $\text{KOH}$ ]; salts ( $\text{CaCl}_2$  and  $\text{KCl}$ ); sulfur; organic matter (sugar, sugarcane leaves, and pineapple leaves); and reducing agents (hydroquinone, hydrazine sulfate, and other reducing agents).

Most of the soil additions are expressed as tons per acre in this study. In the calculations, 2,000,000 pounds of oven-dried soil was considered as equivalent to an acre-foot.

#### EXPERIMENTAL RESULTS

##### *Effect of lime ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) on fixation of manganese*

To determine the effect of lime and dolomite on the fixation of manganese, the soil was heated at 100°C. for 24 hours and cooled. Incremental amounts of lime and dolomite ranging from 0 to 32 tons per acre were applied. The soils



were wetted and stored in the laboratory. Exchangeable manganese was extracted and determined. The results are shown in table 1.

With increasing applications of lime, exchangeable manganese decreases rapidly. Dolomite seems to have the same effect as lime, but its action is not so pronounced and the results are slightly irregular. The dolomite used in this

TABLE 1

*Effect of rates of application of lime and dolomite to Poamoho soil on fixation of manganese*

AMOUNT APPLIED PER ACRE	LIME		DOLOMITE	
	Exchangeable manganese	Manganese fixed over check	Exchangeable manganese	Manganese fixed over check
<i>tons</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	1605	....	1659	....
0.25	1576	29	1659	0
0.5	1461	144	1678	-19
1.0	1368	237	1670	-11
2.0	1195	410	1678	-19
4.0	969	636	1596	63
8.0	656	949	1536	123
16.0	362	1243	1376	283
32.0	148	1457	1324	335

TABLE 2

*Effect of rates of application of lime and dolomite to Poamoho soil on yield and manganese content of cowpeas*

AMOUNT APPLIED PER ACRE	LIME			DOLOMITE		
	Average yield of four replicates	Manganese content	Decrease in manganese content as compared to check	Average yield of four replicates	Manganese content	Decrease in manganese content as compared to check
<i>tons</i>	<i>gm.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>gm.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0.0	2.5	1110	...	2.5	1210	....
0.5	1.4	665	445	3.2	555	655
1.0	2.8	530	580	3.4	650	560
2.0	2.1	425	685	2.9	605	605
4.0	2.0	255	855	2.2	330	880
8.0	2.2	265	845	2.6	210	1000

study was very coarse. This coarseness may explain the weak action. The lime used was in a finely subdivided state.

In the greenhouse work, lime and dolomite were applied in increasing amounts from 0 to 8 tons. The cowpea plants were grown for 20 days, and all the above-ground parts were harvested. The yields and manganese contents are given in table 2.

When lime or dolomite is applied to the soil, absorption of manganese by plants

decreases. These results confirm the findings of the chemical analysis of soils. Generally, lime and dolomite seem to be equally effective in reducing the uptake of manganese by plants. It is interesting to note that the first light application of 500 pounds of either lime or dolomite reduces the uptake of manganese tremendously. With further increase in application, the manganese absorption is reduced gradually.

*Effect of bases and salts on release and fixation of manganese in sterile soil*

Most of the experiments in this study were done under nonsterile conditions. One experiment, however, was conducted under aseptic conditions to determine whether fixation or release of manganese could take place in absence of bacterial action. Increasing amounts of calcium hydroxide, sodium hydroxide, potassium

TABLE 3

*Effect of bases and salts on release and fixation of manganese in sterile Poamoho soil*

AMOUNT APPLIED PER ACRE	Mn IN SOIL TREATED WITH				
	Ca(OH) <sub>2</sub>	NaOH	KOH	CaCl <sub>2</sub>	KCl
<i>tons</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	554	554	554	554	554
0.25	...	480	550	...	...
0.5	...	512	524	540	540
1.0	403	424	490	572	545
2.0	300	360	420	602	554
4.0	192	290	364	710	550
8.0	145	...	...	720	...
16.0	96	...	...	...	...

hydroxide, calcium chloride, and potassium chloride were added to Poamoho soil in Erlenmeyer flasks. The soils were moistened, and the flasks were tightly stoppered with cotton plugs. The soils were autoclaved for 15 minutes at 15 pounds' steam pressure and were then stored in the laboratory for the customary 2 weeks. The manganese was extracted with normal ammonium acetate solution, and the extracts were analyzed for manganese.

The results are shown in table 3. Increasing applications of all the bases [Ca(OH)<sub>2</sub>, NaOH, and KOH] decreased the manganese level. Calcium chloride increased the manganese level. Potassium chloride, on the other hand, seemed to have no effect.

*Effect of sulfur on release of manganese*

Sulfur was added to the Poamoho soil in increasing amounts from 0 to 4 tons per acre. After the usual moistening and holding of the soil, the exchangeable bases were extracted, and manganese was determined in the extract. The results, in table 4, show that addition of sulfur releases manganese. This study was also extended to greenhouse work. The results are shown in table 5.

Although the increase in exchangeable manganese due to application of sulfur is not marked, the increase in the manganese content of the plant is surprisingly great.

TABLE 4  
*Effect of rates of application of sulfur to Poamoho soil on release of manganese*

SULFUR APPLIED PER ACRE	EXCHANGEABLE MANGANESE	MANGANESE RELEASED OVER CHECK
<i>tons</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0.0	7.8	....
0.5	12.4	4.6
1.0	16.2	8.4
2.0	29.1	21.3
4.0	39.9	32.1

TABLE 5  
*Effect of rates of application of sulfur to Poamoho soil on yield and manganese content of cowpeas*

SULFUR APPLIED PER ACRE	AVERAGE YIELD OF FOUR REPLICATES	MANGANESE CONTENT	INCREASE IN MANGANESE CONTENT OVER CHECK
<i>tons</i>	<i>gm.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0.0	3.3	1320	....
0.5	2.6	2620	1300
1.0	2.2	3250	1930
2.0	2.3	6940	5620
4.0	1.6	9000	7680
8.0	1.4	9000	7680

*Effect of organic matter on release of manganese*

The organic matter used in this study comprised sucrose, ground pineapple leaves, and ground sugarcane leaves, all of which have high carbon-nitrogen ratios and when placed in soils increase biological activity.

Sugar was added to the soil in incremental amounts, and the soil was moistened and allowed to stand in the laboratory for 1 week. The results of the analysis are shown in table 6. Pineapple leaves and sugarcane leaves were added separately to the soil and were given the same treatments as the experiment with sugar. The soils were sampled at intervals and manganese analyses made. The amounts of pineapple and sugarcane leaves applied to the soil were extremely high in some cases. These large amounts were tried because the plant residues left in the field are high after certain crops are harvested. Some workers have estimated that the above-ground residual parts of pineapples, for example, may exceed 100 tons per acre. Table 7 gives the results after the application of pineapple leaves and sugarcane leaves.

Tables 6 and 7 clearly show that with increasing applications of sugar, pineapple leaves, or sugarcane leaves, the level of exchangeable manganese increases. With the pineapple and sugarcane leaves, release of manganese takes place very rapidly, in fact it is evident after 24 hours. Upon further standing of the soil, the

TABLE 6

*Effect of rates of application of sugar to Poamoho soil on release of manganese*

SUGAR APPLIED PER ACRE	EXCHANGEABLE MANGANESE	MANGANESE RELEASED OVER CHECK
<i>tons</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0.0	5.1	....
0.5	6.1	1.0
1.0	6.3	1.2
2.0	7.3	2.2
4.0	135.9	130.8
8.0	118.6	113.5
16.0	466.7	461.6

TABLE 7

*Effect of rates of application of pineapple and sugarcane leaves to Poamoho soil on release of manganese*

AMOUNT APPLIED PER ACRE	EXCHANGEABLE MANGANESE IN SOIL TREATED WITH PINEAPPLE LEAVES			EXCHANGEABLE MANGANESE IN SOIL TREATED WITH SUGARCANE LEAVES		
	1st day	7th day	19th day	1st day	7th day	19th day
<i>tons</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	37.8	16.6	6.5	38.5	30.4	3.7
1	43.0	22.5	7.3	40.6	34.6	6.7
2	51.7	35.7	7.3	46.8	47.3	18.3
4	73.7	53.6	54.8	52.8	85.3	19.3
8	119.3	164.8	1828.6	59.0	811.2	308.6
16	203.1	152.2	192.8	112.9	114.4	78.0
32	307.1	1936.0	2801.3	165.5	217.7	445.8
64	437.6	2596.2	3078.3	349.1	951.3	2853.3
128	586.7	3526.5	3593.8	415.0	1507.1	4693.3
256	765.1	924.9	3102.9	550.9	666.7	3342.2

TABLE 8

*Effect of rates of application of sugarcane leaves to Poamoho soil on yield and manganese content of cowpeas*

SUGARCANE LEAVES APPLIED PER ACRE	AVERAGE YIELD OF FOUR REPLICATES	MANGANESE CONTENT	INCREASE IN MANGANESE CONTENT OVER CHECK
<i>tons</i>	<i>gm.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	2.5	960	....
1	2.2	1240	280
2	2.5	1150	190
4	2.3	1260	300
8	1.8	1625	665
16	1.5	1550	590
32	1.5	1800	840
64	1.0	3130	2170

exchangeable manganese increases to extremely high levels with the higher applications of organic matter. In the lower treatments of pineapple and sugarcane leaves, the level of exchangeable manganese at first increases and then gradually

decreases. The same behavior would probably be true for the higher applications, if the experiments were carried out for longer periods.

Table 8 shows that addition of sugarcane leaves to soil increases the manganese absorption by cowpea plants. It seems logical to assume that pineapple leaves and sugar would have the same effect; therefore, no pot experiments were performed for either.

#### *Effect of reducing agents*

The soil treatments up to this point have been those normally used in agricultural practices. For better understanding of the manganese question, treatments not ordinarily used in agricultural practices and some that are agriculturally not feasible were studied next. In this series of experiments various reducing agents, including hydroquinone, stannous chloride, formaldehyde, hydrazine sulfate, and potassium iodide, were used. Pineapple leaves were also included

TABLE 9  
*Effect of reducing agents on manganese in Aiea soil*

TREATMENT	EXCHANGE- ABLE MANGANESE	HYDRATED FORM OF MANGANESE	TOTAL EXTRACTED MANGANESE	INCREASE IN EX- CHANGEABLE Mn OVER CHECK	INCREASE IN HY- DRATED FORM OF Mn OVER CHECK	INCREASE IN TOTAL Mn EX- TRACTED OVER CHECK
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
None.....	4.1	522.7	526.8	....	....	....
0.2 gm. Hydroquinone.....	225.8	727.7	953.5	221.7	205.0	426.7
0.5 gm. Stannous chloride.....	9.7	648.4	658.1	5.6	125.7	131.3
0.5 gm. Formaldehyde.....	194.6	704.3	898.9	190.5	181.6	372.1
0.2 gm. Hydrazine sulfate.....	92.1	817.2	909.3	88.0	294.5	382.5
0.2 gm. Potassium iodide.....	13.5	572.8	586.3	9.4	50.1	59.5
5 gm. Pineapple leaves.....	569.1	1270.7	1839.8	565.0	748.0	1313.0

in this study, because the action of any organic matter with a high carbon-nitrogen ratio is one of reduction.

One hundred grams of the soils were treated with the various reducing agents, moistened, and stored for 3 weeks. The soils were stirred at intervals, and water was added from time to time to maintain the initial moisture content. Extractions, oven-drying, and reextraction followed the procedure previously outlined. The manganese in the second extract is considered as the manganous oxide which became soluble as a result of the splitting of the complex hydrated oxide,  $(\text{MnO})_x \cdot (\text{MnO}_2)_y \cdot (\text{H}_2\text{O})_z$ , by heating (5). This set of experiments was performed on the Poamoho, Aiea, Koko Head, and Manoa soils. Because the results were similar, only those for the Aiea soil are given (table 9). Addition of reducing agents increased the amounts of exchangeable, hydrated, and total manganese extracted.

#### DISCUSSION AND CONCLUSION

The experimental results showed that the level of exchangeable manganese was decreased in the soil, and the amount of plant absorption of manganese was decreased by application of lime, dolomite, calcium hydroxide, sodium hydroxide,



and potassium hydroxide to the soil. Sherman and Harmer (25), Leeper (15), and others believe that the fixation of manganese is brought about by oxidation of manganous manganese. Sherman and Harmer (25) also observed that neutral and alkaline conditions favor formation of manganic manganese, and acid conditions favor formation of manganous manganese.

When a manganous salt is dissolved in water, no oxidation of the manganous ion takes place, and the solution remains stable indefinitely if no oxidizing agent is added to the solution. Oxygen in the air apparently does not oxidize the manganous ion in a water solution. The same holds true for an acidic solution of a manganous salt. Nichols and Walton (23), in their study of the autoxidation of manganous hydroxide, added sodium hydroxide and other bases to a solution of a manganous salt and ammonium chloride. The ammonium chloride was present in the solution to prevent the precipitation of manganous hydroxide. They noticed that the oxidation of the manganous hydroxide by oxygen proceeded slowly at first and increased in reaction rate later when the higher oxides precipitated. They were able to establish that the presence of certain finely divided substances in the reacting medium accelerated the reaction rate. They attributed this to a surface catalytic effect. Mellor (21, pp. 139-464), in his comprehensive review, showed that when a base is added to a solution of a manganous salt, manganous hydroxide forms as a white gelatinous precipitate. The fine state of subdivision of the manganous hydroxide favors its rapid oxidation to the hydrated dioxide form. The conclusions to be drawn from these studies are that the oxidation of the manganous ion by oxygen can take place in a basic medium and that the presence of certain finely divided substances will catalytically increase the rate of oxidation.

Lime and dolomite, when added to the soil, raise the pH and bring about conditions that favor oxidation of manganese. Oxidation proceeds rapidly because soil consists of finely divided particles which will accelerate the rate of reaction. At the same time, lime and dolomite will increase the hydroxyl-ion concentration to a point where the solubility product of manganous hydroxide is exceeded. When the solubility product is exceeded, manganous hydroxide precipitates in a finely divided state, which will favor its rapid oxidation. In this way chemical fixation of manganese takes place when lime, dolomite, or other basic constituents are added to the soil.

When sulfur was added to the soil, the exchangeable manganese content was increased. It was shown also that the plant uptake of manganese was increased. Waksman (30) has shown that when sulfur is added to soils, the sulfur is rapidly oxidized principally by biological processes to sulfuric acid. Sulfuric acid would naturally lower the pH of the soil and bring about conditions for the reduction of the higher oxides of manganese, as indicated previously. The reduction of the higher oxides of manganese would make manganese more available in the soil.

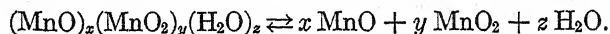
When calcium chloride was added to the soil, the level of exchangeable manganese was increased. The slight acidity of a solution of this salt would lead to a release of manganese. Because a solution of potassium chloride is nearly neutral in reaction, it will neither increase nor decrease exchangeable manganese.

It has been shown that addition of organic matter with a high carbon-nitrogen

ratio will increase the availability of manganese in soil. Organic matter with a high carbon-nitrogen ratio contains large amounts of easily oxidizable substances such as starch and sugar. When these substances are added to the soil in the form of residual plant parts, biological oxidation of the organic matter takes place with the formation of carbon dioxide. Leeper (15) has said, "Biological reduction can take place at any pH value if the oxygen tension is low, when the anaerobic bacteria use the higher oxides as a source of oxygen." Reduction of the higher oxides takes place when the biological oxidation of organic matter proceeds at so rapid a rate that the air cannot supply oxygen in adequate amounts. When this occurs, reduction of the higher oxides takes place to supply the needed oxygen. This leads to an increase in the available manganese.

The experimental results show that reducing agents increase the exchangeable and the hydrated forms of manganese. The reduction by the various reducing agents is a straightforward chemical reduction, which needs no discussion. The hypothesis of the hydrated form of manganese oxide and the release of available manganese by dehydration is a new concept, which was proposed by Fujimoto and Sherman (5) as a possible explanation for their experimental findings.

This postulate states that a certain portion of the manganese in the soil exists as a complex, hydrated oxide of the following type:  $(\text{MnO})_x(\text{MnO}_2)_y(\text{H}_2\text{O})_z$ . When the water of hydration is split off, the rest of the molecule becomes unstable and breaks up into its component parts—manganous oxide and manganese dioxide. The manganous oxide then may go into solution and become available for absorption by plants. The reaction can be represented by the following chemical equation:



The proponents of this concept also suggest that this reaction may be reversible.

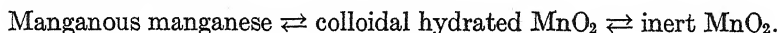
Nichols and Walton (23) showed that when manganous hydroxide was oxidized by oxygen in a basic medium, complete oxidation to the dioxide state was not possible under their experimental conditions. They found that the final volume of oxygen absorbed varied from 67 to 83 per cent of the volume theoretically required for the formation of manganese dioxide. Meyer and Nerlich (23) found in their work that the volume of oxygen absorbed varied between 81 and 94 per cent of the amount corresponding to the formation of manganese dioxide. Herman and Lievin (23) were unable to observe an absorption of more than 82 per cent of the theoretical volume of oxygen necessary for the formation of manganese dioxide. Nichols and Walton concluded that the higher oxides of manganese exist in the following forms:  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ . Naftel (22) showed that  $\text{Mn}_2\text{O}_3$  exists in the soil. Dion and Mann (3) concluded from titration experiments that trivalent manganese exists in the soil.

It has been shown that the manganese oxides exist in varying degrees of oxidation and can be arranged in progressively higher states of oxidation in the following manner:  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ . The existence of divalent and tetravalent manganese is well established. If the valences of  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  are calculated, the values of  $2\frac{2}{3}$  and 3 are obtained respectively. Because the val-

ences of the intermediate manganese oxides are not well established, no valence values will be given for the intermediate compounds. Instead, the writers will use the formula,  $(\text{MnO})_x(\text{MnO}_2)_y$ , to represent  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and any other oxide the state of oxidation of which is between the divalent and tetravalent forms of manganese. This formula is used also because it seems to represent the behavior of manganese in soils satisfactorily.

Judged from all observable data, three basic forms of manganese apparently exist in the soil from the standpoint of availability to the plant. The manganous ion or the manganous oxide is readily available to plants. The hydrated form is not readily available but becomes available with changes in physical conditions in the soil, especially changes in temperature and water content. The third is the difficultly available form, manganese dioxide, which becomes available only after drastic changes in the soil.

Leeper (13) classified the manganese in soils into the manganous manganese; the colloidal hydrated manganese dioxide, which is easily reducible; and the inert manganese dioxide. He has suggested a new hypothesis in which the various forms of soil manganese would exist in an equilibrium, which can be expressed by the following equation:



In a later paper, Leeper (15) speaks of the maganic oxides or the higher oxides which include  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnO}_2$ . He reports that a certain portion of the maganic oxide is easily reducible and the rest of the maganic oxide is inert.

More recently, Dion and Mann (3) have proposed a manganese cycle based on the oxidation-reduction equilibrium between divalent and tetravalent manganese oxides and the existence of a trivalent manganese oxide which undergoes dismutation to give both divalent and tetravalent manganese. The term "dismutation" apparently means an oxidation-reduction of the trivalent manganese with divalent and tetravalent manganese forming as products of the reaction. This reaction is similar to the Cannizzaro reaction in organic chemistry. By bubbling air through a solution containing manganous chloride, ammonium chloride, and ammonium hydroxide, these investigators have precipitated an oxide, which they say is  $\text{Mn}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . They also report that dismutation takes place under acidic conditions. The authors of this paper have precipitated  $\text{Mn}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , according to the method of Dion and Mann, and have found that this compound does not behave in the same manner as the manganese in Hawaiian soils when subjected to certain physical treatments. Because of this discrepancy, it is felt that two entirely different phenomena are dealt with here.

With the foregoing considerations, it seems possible now to introduce a new hypothesis on the manganese cycle in the soil. Figure 1 is a graphic representation of the authors' concept of the actual behavior of the various forms of manganese in the soil.

In the soil, two processes that influence the availability of manganese are in motion: the first is the oxidation-reduction process, and the second is the hydration-dehydration process of the manganese oxide. The oxidation-reduction sys-

tem determines the relative amounts of manganous oxide and manganese dioxide. This can be readily seen in the upper horizontal part of the illustration. When free manganous oxide, manganese dioxide, and water are present in the soil, addition and hydration of the oxides will take place with the formation of a complex hydrated manganese oxide, as shown in the lower portion of the illustration. From all indications, this form of oxide is stable when moisture is present and the temperature is low. When the soil becomes dry and the soil

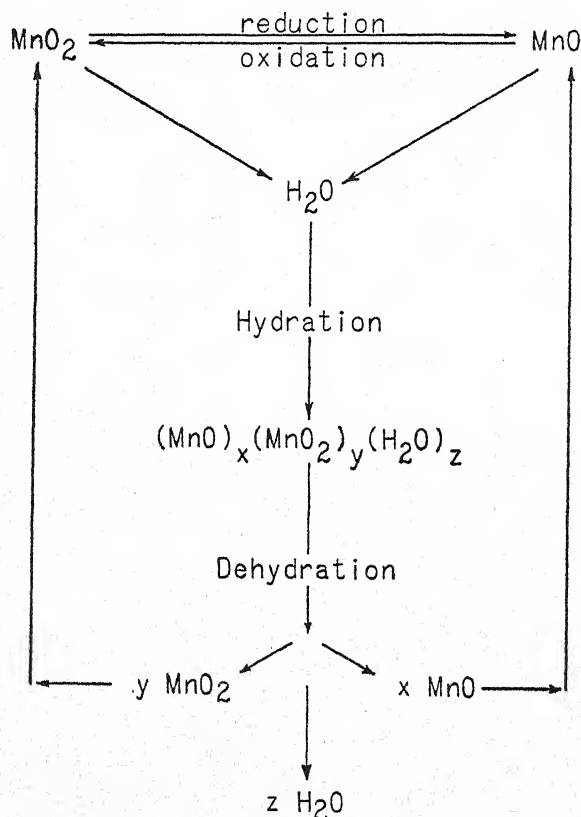


FIG. 1. THE MANGANESE CYCLE IN SOIL

temperature rises, this form of oxide breaks up into its component parts. The component parts can then come under the influence of either one of the two processes, or one of the components (manganous oxide) may be taken up by plants. In this way the manganese cycle in the soil is realized.

The manganese cycle as illustrated can be utilized in understanding how to influence the manganese status in soils. The point where control can be most effectively used is at the oxidation-reduction portion. In Hawaii, because of the high manganese content of the soil, the aim would naturally be to reduce the availability of manganese. This can be done by bringing about conditions that



would allow oxidation to take place more readily. To do this, lime, dolomite, or any other soil treatment that would raise the pH of the soil can be added. On the other hand, acid-forming substances and reducing agents should not be applied to manganiferous soils. Organic matter, especially forms with a high carbon-nitrogen ratio, should not be applied and intimately mixed with the soil. If reducing agents are kept out of the soil, and the pH of the soil is raised, the manganous form of manganese will rapidly be oxidized to the dioxide form, which is not available to plants. At the same time, any manganous oxide, released by the dehydration of the complex hydrated oxide, will be oxidized to the dioxide form. In this way even the potentially available form (hydrated oxide) will be reduced in the soil.

There is another point at which control of the availability of manganese can be exercised. This can be done by influencing the hydration or dehydration of the manganese oxides. In the field, rainfall and temperature cannot be controlled. The degree of wetness and the soil temperature, however, can be influenced to a certain degree. Surface mulching will influence the soil temperature and the rate of evaporation of moisture from the soil. Irrigation also will change the moisture relations in the soil. When the soil is kept moist and cool, hydration of the manganese oxide will take place. This will lead to a lower availability of manganese.

In agricultural practices, complete control of the availability of soil manganese cannot be expected. Judicious application of the hypothesis of the manganese cycle in soils and the methods of influencing the cycle, however, may prove highly profitable.

#### SUMMARY

A study was made of the effect of various chemical treatments upon the fixation and release of manganese in Hawaiian soils. The results may be summarized as follows:

Application of lime, dolomite, and bases resulted in the fixation of manganese in the soil. Plant absorption of manganese was decreased by treatment of soil with lime or dolomite.

Sulfur, when applied to soils, increased the exchangeable manganese and increased the absorption of manganese by plants.

Addition of organic matter (sugar, sugarcane leaves, and pineapple leaves) to the soil resulted in an increase in exchangeable manganese and in plant absorption of manganese.

Chemical reducing agents increased the level of exchangeable and hydrated forms of manganese.

A new hypothesis on the manganese cycle in soils is presented. The manganese cycle is based on the oxidation-reduction system and the hydration-dehydration system in soils.

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# MAGNESIUM IN FERTILIZERS, SOIL AMENDMENTS, AND MANURES

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Important changes have occurred with the passage of time in the sources of magnesium as a plant food for growing crops. A previous paper (19) gave the results of a study of these changes from 1850 to 1937. Further important changes have occurred since then. It is the purpose of this paper to review briefly some of the earlier developments in the light of present conditions and to outline the developments since 1937.

## FERTILIZERS

The present widespread practice of adding special magnesium-containing materials to fertilizer mixtures has developed within the last 20 years. Dolomite is by far the most important of these materials, but various other materials have also been employed, especially in recent years. Most of these materials not only supply plant-nutrient Mg, but serve the further useful purpose of reducing soil acidity. Both uses are important to agriculture.

The chief reasons for the rapid development of the practice of adding magnesian materials to fertilizers are (a) a rapid decrease after 1915 in the use of natural organic by-products and kainite as fertilizers; (b) discoveries in 1922 and later years that certain symptoms in plants are due to Mg deficiency; (c) a rapid increase in the physiological acidity of mixed fertilizers after 1928; and (d) a desire to replace sand with some other cheap, but more useful filler.

The trend toward use of the by-product natural organics, such as tankage and fish scrap, for feeds rather than fertilizers, which started about 1900 and became noticeable in 1915, has continued to the present. Very little such material, except in forms that are unsuitable for feed, such as castor pomace, sewage sludge, and process tankage (feathers, leather scrap, etc.), is now used as fertilizer. Most of these organics contain 0.5 to 1.2 per cent MgO. Kainite and manure salts, which in the early part of this century provided nearly all of our fertilizer potash, have nearly disappeared from the market. The old-style kainite, which until 1915 supplied the bulk of our potash in fertilizers, has entirely disappeared. This material contained as much MgO as K<sub>2</sub>O. As a result of these changes, the average MgO content of all fertilizers dropped from 1.39 per cent in 1910 to 0.90 per cent in 1920 and to 0.72 per cent in 1930.

<sup>1</sup> Credit is due Hilda M. Wallace, for assistance in the computations, and Henry A. Huschke, director, Agricultural Limestone Division, National Crushed Stone Association, Washington, D. C., for assistance in the preparation of table 3.

<sup>2</sup> Division of Fertilizer and Agricultural Lime, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, Beltsville, Maryland.

Symptoms of magnesium deficiency became more widespread in crops after 1915, but were not understood at that time. For instance, farmers believed that red-leaf in cotton was due to insufficient potash, because it always responded to applications of kainite. Although Mg had long been known by scientists to be an essential plant nutrient, there was no easy way, until 1922, of recognizing where it was deficient in the soil. Then Garner, McMurtrey, and Moss (9) proved that sand-drown of tobacco was due to lack of Mg. In the next few years, Mg-deficiency symptoms in a variety of plants began to be recognized for what they were. This knowledge made it easier to see where Mg is needed and increased the demand for the nutrient.

Until about 1928, mixed fertilizers were made from so varied a combination of materials that they had no appreciable effect on soil acidity. Then the introduction of soluble forms of nitrogen at low costs per unit greatly stimulated use, in the manufacture of fertilizers, of acid-forming materials and discouraged use of materials that produce bases in the soil. Pierre (29) was one of the first to recognize the unfavorable consequences to agriculture of these trends and suggested the advisability of adding lime or basic slag in the preparation of mixed fertilizers to counteract the acid-forming tendency. MacIntire and Sanders (11) in 1928 suggested the use of dolomite for this purpose and emphasized its advantages over other proposed materials. In 1933, Mehring and Peterson (17) reported that the effect of the average mixed fertilizer on the soil in 1932 was strongly acid as compared with a mean basic reaction 30 years earlier. Parker (26) played an important part in developing these ideas and getting the industry to add dolomite to fertilizers in more adequate amounts.

The earliest reference to use of limestone in the manufacture of fertilizers seems to have been in 1913 by Brogdon (4). The Dunn Oil Mill of Dunn, North Carolina, is known to have started to mix dolomite in fertilizers about 1915. By 1920 at least three limestone producers were selling dolomite to fertilizer manufacturers in the southeastern states. These manufacturers, in using dolomite, had two purposes: one, to neutralize the acidity of superphosphate and thus to reduce bag-rotting; and the other, to provide a filler in mixed fertilizers that was less objectionable than sand. The idea of caring for soil acidity and supplying plant-nutrient Mg through the fertilizer, however, was not appreciated at that time.

After 1928 the usage of dolomite in the manufacture of fertilizers increased rapidly until 1937. Since then, the tonnage has fluctuated. About 331,000 tons of dolomite was used in the manufacture of fertilizers in 1940. This is 6 per cent of the tonnage of mixed fertilizers. In 1946 the consumption was 554,000 tons, or 5 per cent of the total. All limestone used at present in the manufacture of mixed fertilizers is of the dolomitic variety, although some high-calcic limestone was thus used many years ago. High-calcic limestone proved unsatisfactory because it drove off ammonia, under certain circumstances, and reverted part of the available  $P_2O_5$ , under others, whereas dolomite ordinarily does not do either.

During the recent war the International Minerals and Chemical Corporation



started production of sulfate of potash-magnesia at Carlsbad, New Mexico. This has become an important source of plant-food MgO in fertilizers. From 1935 to 1939, the most important source of MgO, other than dolomite, added to fertilizers was calcined kieserite ( $\text{MgSO}_4$ ), also known as Emjeo. When importations of this material from Germany were stopped by the war, actual magnesia and other materials were produced in this country as substitutes. The consumption of all these materials in 1946 totaled about 26,000 tons, of which actual magnesia constituted 39 per cent. Seven companies are now supplying magnesia for use in the manufacture of fertilizers. Seawater magnesia, Solmago, Kemidol, and Michox are trade names for some of these products. Some other materials used in the manufacture of fertilizers as sources of Mg are magnesite ( $\text{MgCO}_3$ ), calcined brucite [brucite is  $\text{Mg}(\text{OH})_2$ ]; selectively calcined dolomite, also known as Actomag ( $\text{MgO} \cdot \text{CaCO}_3$ ); and epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). Cal-nitro and A-N-L are mixtures of ammonium nitrate and dolomite.

The reasons for the outstanding usage of dolomite as compared with other sources of Mg are: (a) It is relatively much cheaper; (b) under acid soil conditions it is often just as satisfactory a source of plant-food Mg as the more expensive forms; and (c) it neutralizes acids, which some of the other Mg sources, such as epsom salt, will not do. There are conditions, however, under which use of other sources of Mg than dolomite is necessary for best results in growing crops, as for example, in neutral or alkaline soils deficient in Mg.

Many materials not thought of as sources of Mg, but which are used for their content of the principal plant nutrients, nevertheless do supply significant amounts of Mg. All of the fertilizer phosphates, except ammonium phosphate, contain small percentages of Mg. Open-hearth basic slag usually contains 4 to 7 per cent MgO.

#### *Availability*

The Mg contained in potash salts and in the sulfate form is immediately available to plants when placed in the soil.

Magnesia is only slightly soluble in water, but sufficiently so to be available to plants in neutral or acid soils. When magnesia is added to fertilizer mixtures containing superphosphate it reacts in part to form highly soluble salts. If too much is added these reactions result in serious reversion of phosphate or loss of ammonia. Under most conditions, provided the storage temperature does not rise above  $60^\circ\text{C}$ ., up to 40 pounds of magnesia may be added without loss of other plant-food values. Such a mixture cannot be ammoniated without reversion. According to Whittaker, Rader, and Zahn (38), as much as 80 pounds of magnesia may be added under favorable circumstances without serious loss. With quantities up to 80 pounds, 70 to 90 per cent of the MgO will be rendered highly soluble in water.

Dolomite is relatively insoluble in water, but its Mg is available to plants in most acid soils. It also reacts in mixtures with superphosphate to form water-soluble compounds, but the reactions are much slower than is the case with

magnesia. A much larger quantity of dolomite may be added without danger of reversion or loss of ammonia.

Further details on availability of Mg in various materials to crops and on the chemistry of such materials in fertilizer mixtures are reported by MacIntire and Shaw (12), MacIntire and Shuey (13), Beeson and Ross (3), and Whittaker and Ross (39).

#### *Magnesia content*

The average MgO content of each kind of material employed in the manufacture of fertilizers is given in table 1.

The companies selling dolomite to fertilizer manufacturers supplied the author with the average analysis of their product as well as of the tonnage sold. The weighted average MgO contents are 19.37 and 19.63 per cent for 1938 and 1945, respectively. Pure dolomite contains 21.83 per cent MgO. Commercial brands vary from 18.34 to 21.1.

Mixed fertilizers in 1910 contained on the average 2.28 per cent MgO, none of which was derived from material added deliberately for the purpose of supplying MgO. By 1930 the average had dropped to 1.09 per cent, of which 0.26 per cent was in the form of dolomite. In 1937, mixed fertilizers contained 1.95 per cent MgO, of which 1.26 per cent came from dolomite and 0.07 per cent from calcined kieserite. In 1945, the mean MgO content of commercial mixtures had increased slightly to 2.07 per cent, of which 1.08 per cent was supplied by dolomite and 0.16 per cent by magnesia. Mixed fertilizers now provide, therefore, about 90 per cent as much MgO per pound of fertilizer as they did before 1915.

Fertilizers prepared for potatoes and tobacco are more likely to contain quantities of Mg added especially to ensure an adequate supply than are fertilizers sold for general crops. For example, of the tobacco grades analyzed by the North Carolina Department of Agriculture (24) in 1945, 71 per cent were guaranteed to contain specified quantities of MgO, but of the general crop fertilizers, only 16 per cent were guaranteed to contain MgO.

The control laboratories of Florida (32), Maine (33), Massachusetts (15), New Hampshire (31), New York (22), North Carolina (24), Rhode Island (1), and Virginia (34), have published the results of thousands of determinations of MgO on mixed fertilizers that were guaranteed to contain it. The mean value increased from 2.57 in 1938 to 3.20 per cent in 1946. The quantities most frequently guaranteed, in the order of importance, are 2, 3, 1, 4, 5, 6, and 10 per cent.

Mixed fertilizers sold in the Southeastern States, especially Florida, contain more Mg, and those sold in the North Central States less, on the average than the United States mean value. This should be expected because the soils of the North Central region are generally much better supplied with Mg than those of the Atlantic Coastal Plain. Many farmers in the North Central States lime their soils so heavily that a little Mg more in the fertilizer would have no significance in crop production anyway. Large quantities of animal manures are

applied to the soils in the Midwest also, and these contain significant quantities of Mg.

Even though no recognized Mg-carrier is used in its preparation, a mixed fertilizer is almost sure to contain a small quantity of this element. Smith

TABLE 1  
Average magnesia content of fertilizer materials\*

MATERIAL	MgO	MATERIAL	MgO
	<i>per cent</i>		<i>per cent</i>
<i>Chemical nitrogen</i>		<i>Potash</i>	
Calcium cyanamide.....	0.11	Cement dust.....	2.00
Calcium nitrate.....	2.49	Cotton hull ashes.....	4.94
Cal-nitro.....	7.40	Manure salts, 20%.....	5.92
Potassium nitrate.....	0.81	Manure salts, 25%.....	0.25
Potassium-sodium nitrate.....	0.16	Manure salts, 30%.....	1.53
Sodium nitrate.....	0.10	Muriate of potash, 50%.....	0.63
<i>Natural organics</i>		Muriate of potash, 60%.....	0.09
Castor pomace.....	0.62	Sulfate of potash.....	1.10
Cocoa by-products.....	0.80	Sulfate of potash-magnesia.....	†
Cottonseed meal.....	0.90	Tobacco stems.....	0.60
Dried manures.....	1.20	Vegetable potash.....	4.80
Fish scrap.....	0.47	Wood ashes.....	3.41
Guano.....	0.75	<i>Miscellaneous</i>	
Sewage sludge, activated.....	1.32	Brucite, calcined.....	74.00
Sewage sludge, other.....	0.50	Dolomite.....	19.50
Tankage, animal.....	0.35	Dolomite, selectively calcined...	27.00
Tankage, garbage.....	0.71	Gypsum.....	0.68
Tung meal.....	0.86	Epsom salt.....	16.00
<i>Phosphates</i>		Hydrated dolomitic lime.....	29.00
Ammonium phosphate, 11-48.....	0.64	Kieserite, calcined.....	30.50
Ammonium phosphate, 16-20.....	0.30	Magnesia.....	92.00
Base goods, wet-mixed.....	0.31	Magnesite.....	45.00
Basic slag, open-hearth.....	5.63	Nitrophoska.....	1.89
Bone meal, raw.....	0.82	Peat.....	0.32
Bone meal, steamed.....	0.37	Peanut shells.....	0.24
Calcium metaphosphate.....	0.16	Phosphate rock.....	0.20
Precipitated bone.....	0.40		
Rock phosphate.....	0.25		
Superphosphate, double.....	0.38		
Superphosphate, normal.....	0.47		

\* Materials used in 1946 but not listed do not contain significant quantities of MgO. See also Mehring and Lundstrom (19).

† Imported material 11.45 per cent; domestic 18.5 per cent.

and Deszyck (30) have reported values from 0.11 to 0.87 per cent for such fertilizers, and Lundstrom and Mehring (10) give complete analyses of a number of such goods varying from 0.10 to 0.54 per cent. The average MgO content of 62 such mixed fertilizers is 0.28 per cent.

*Physiological acidity*

Had no dolomite or magnesia been added to mixed fertilizers in 1944, the potential acidity would have been equivalent to 978,000 tons of calcium carbonate. This is equivalent to 230 pounds per ton of mixed fertilizer. When the proper deductions<sup>3</sup> are made for the Mg-materials actually used, it appears that the real acid-forming properties on the average were equivalent to only 103 pounds per ton, or about 45 per cent of what they would have been otherwise.

In 1935, the potential acidity was only 25 pounds per ton (16). Nevertheless, in 1935, mixed fertilizers contained virtually the same percentage of dolomite as in 1944 (about 6 per cent). The reason for this increase in acidity, despite the fact that about the same proportion of neutralizing agents had been added, is that relatively more nitrogen was present in 1944 fertilizers, and almost all of this nitrogen was derived from acid-forming materials, whereas only three-fifths of the nitrogen in 1935 came from acid-forming sources.

Published analyses confirm the idea that commercial mixed fertilizers have become more acid-forming again in recent years. The bulk of the mixed fertilizers sold in Alabama and North Carolina are non-acid-forming. But the average for North Carolina (24) decreased from 60 pounds basic equivalent in 1939 to 35 pounds in 1945. Most of the mixed fertilizers consumed in the Middle Atlantic and New England States are acid-forming and are becoming more so. For example, the average mixed fertilizer in Maryland (14) changed from 61 pounds acid in 1939 to 117 pounds acid in the first half of 1947. A trend toward greater acid-forming properties is evident in the data for all of the five states that publish such figures.

SOIL AMENDMENTS<sup>4</sup>

For centuries, lime has been used as a soil amendment, but previous to 1900 it was believed that it must be in the caustic form, that any lime containing over 10 per cent MgO was poor, and that one with more than 25 per cent was worthless. Patterson (27) reporting, in 1900, a series of experiments on the use of soil amendments said, "The total yields obtained with the five crops give some peculiar and unexpected results, which cannot be explained by the ordinary and commonly accepted notions as to the action and effects of lime." These unexpected results were that lime in the form of carbonate was as good as the oxide or hydroxide and that magnesium lime, which at that time was commonly believed to be poisonous to the soil and crop, gave the highest yield.

Prior to 1910, less than a million tons of liming materials were used annually

<sup>3</sup> Commercial dolomite and magnesia have acid-neutralizing powers about 98 and 240 per cent, respectively, of that of pure calcium carbonate.

<sup>4</sup> In the earlier study (19), such materials as gypsum, wood ashes, peat, seaweed, phosphate rock, and sulfur were classified as miscellaneous soil amendments. In other publications of this division these materials when sold commercially have been included with fertilizers. In order that the results of this study may be comparable with those of the earlier study, the old classification is used here.



in American agriculture. Most of this was burned lime or hydrated lime, and virtually all of it was high-calcic material. Consumption increased very gradu-

TABLE 2  
*Estimated average MgO content of liming materials, by states, 1946*

STATE AND REGION	SOURCE OF DATA*	LIME-STONE	BURNED LIME	HY-DRATED LIME	STATE AND REGION	SOURCE OF DATA*	LIME-STONE	BURNED LIME	HY-DRATED LIME
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Maine.....	(33)	12.65	†	9.84	Illinois.....	(35)	10.36	†	†
New Hampshire..	(31)	5.50	7.00	9.00	Michigan.....	(5)	3.50	†	4.00
Vermont.....	(36)	5.41	5.00	2.98	Wisconsin.....	(5)	20.73	†	25.00
Massachusetts...	(15)	13.27	13.00	12.56	East North Central....		10.40	†	19.95
Rhode Island....	(1)	12.57	†	9.33					
Connecticut.....	(2)	15.48	26.27	25.32	Kentucky.....	(5)	.85	1.50	1.50
New England..		11.08	20.00	12.61	Tennessee.....	(5)	7.50	14.00	9.00
New York.....	(23)	8.18	14.00	11.29	Alabama.....	(5)	18.00	18.00	20.00
New Jersey.....	(7)	13.96	20.00	13.94	Mississippi.....	(5)	18.00	18.00	20.00
Pennsylvania....	(28)	3.97	4.08	7.55	Louisiana.....	(5)	1.00	†	2.00
Delaware.....	(8)	6.10	15.00	12.99	Arkansas.....	(6)	4.15	†	†
Maryland.....	(14)	6.04	10.25	10.07	Oklahoma.....	(5)	1.25	†	2.00
West Virginia...	(37)	3.91	10.00	13.02	Texas.....	(5)	.30	†	.50
Middle Atlantic.		5.90	9.89	10.03	South Central		5.00	13.05	10.00
Virginia.....	(34)	8.22	3.10	6.44	Minnesota.....	(5)	10.00	†	†
North Carolina..	(24)	18.76	16.50	15.40	Iowa.....	(5)	2.51	†	†
South Carolina...	(5)	16.50	16.00	18.00	Missouri.....	(5)	10.73	†	†
Georgia.....	(5)	15.00	18.00	17.00	Kansas.....	(5)	3.16	†	†
Florida.....	(32)	16.91	18.00	18.00	West North Central....		5.87	†	†
South Atlantic.		13.94	5.11	9.51					
Ohio.....	(25)	10.96	†	26.42	Washington.....	(5)	5.00	7.00	6.00
Indiana.....	(5)	3.95	†	4.50	Oregon.....	(5)	5.00	7.00	6.00
					California.....	(5)	3.50	6.00	5.00
					Western.....		4.56	6.00	5.20
					United States...		8.40	9.14	10.96

\* See "References" at end of paper. Henry Huschke, National Crushed Stone Association, assisted in estimating the values by supplying information on the sources of limestone being utilized in the various states and, in case both high- and low-Mg stones were consumed in the same state, the approximate proportions of each.

† Little or none used. No data available.

ally to 3,500,000 tons in 1935. By that time, usage had switched largely to ground limestone, and the prejudice against Mg-containing forms had disappeared.



The Soil Conservation Program of the U. S. Department of Agriculture began in 1936 and alone consumed 3,720,055 tons of limestone in that first year. In the last 5 years this program has provided farmers with about 20,000,000 tons of limestone annually. Total consumption in 1946 was 29,500,000 tons. Most of this was disposed of in the Northern and Central States. The former prejudice against magnesian forms of liming materials has been replaced in recent years by an actual preference for these forms by many farmers.

The estimated MgO contents of the ground limestone, burned lime, and hydrated lime applied directly to the soil in recent years are given by states in table 2. The mean MgO content of marl applied to the soil is about 1.20 per cent.

The annual reports of the National Lime Association (21) on the consumption of liming materials in agriculture show a tonnage of miscellaneous materials. The bulk of this tonnage consists of crushed oyster, clam, mussel, and egg shells; blast furnace slag; lead-mine chats; and wastes from various industrial plants, such as beet-sugar refineries and paper mills. In this report an average MgO content of 0.50 per cent is assumed for this class of materials.

The weighted average MgO content of all liming materials consumed in the United States is different in each year, but was about 8 per cent in every year since 1937. It was 8.01 per cent in 1938 and 8.20 per cent in 1946.

#### MANURES

Other than the soil itself, the principal source of MgO for growing crops was animal manures until modern times. The number of horses and mules on United States farms has been declining for years, but the numbers of other animals have been increasing. The total production of manures, therefore, has changed very little. The quantities applied to agricultural land were estimated as outlined in the earlier report (19).

The mean MgO contents of various farm manures are as follows:

	<i>per cent</i>
Cattle.....	0.19
Horse.....	0.18
Poultry.....	0.72
Pigeon.....	0.50
Sheep.....	0.22
Swine.....	0.05

#### AGRICULTURAL CONSUMPTION

From 1900 to 1933, total applications of MgO in fertilizers, liming materials, and manures remained fairly constant at approximately 1,200,000 tons annually. The quantities consumed in 1935 and subsequent years are shown in table 3, together with those for a few earlier years. Comparison of these figures shows that consumption has increased rapidly since 1935. It is now about threefold what it was then.

The bulk of the increase is due principally to greatly increased liming of the soil and to wider use of dolomitic limestone for this purpose. Up to 1920,

TABLE 3

*MgO added to United States soils in certain years, by class of material*

YEAR	FERTILIZERS*	LIMING MATERIALS†	MANURES‡	MISCELLANEOUS§	TOTAL
	<i>tons</i>	<i>tons</i>	<i>tons</i>	<i>tons</i>	<i>tons</i>
1910	78,525	58,196	983,000	70,000	1,190,000
1920	65,163	107,073	1,069,000	87,000	1,328,000
1930	61,128	186,386	960,000	56,000	1,264,000
1935	85,719	215,733	960,000	60,000	1,321,000
1936	91,621	465,705	962,000	52,000	1,571,000
1937	114,402	500,809	947,000	52,000	1,614,000
1938	103,196	542,349	933,000	55,000	1,633,000
1939	104,666	633,351	950,000	58,000	1,746,000
1940	108,642	1,070,409	992,000	60,000	2,231,000
1941	123,077	1,072,382	1,003,000	65,000	2,263,000
1942	122,565	1,549,915	1,053,000	60,000	2,786,000
1943	150,191	1,515,611	1,114,000	55,000	2,835,000
1944	176,422	2,156,537	1,153,000	49,000	3,535,000
1945	190,097	1,837,770	1,082,000	45,000	3,155,000
1946	206,050	2,405,311	1,062,000	50,000	3,723,000

\* Calculated from tonnages of each kind of material consumed (19, 20) and its MgO content, table 1.

† From Natl. Lime Assoc. Rpts. (21) and figures in table 2.

‡ From numbers of animals on farms, Agricultural Statistics, the annual production per animal as given by Van Slyke (Fertilizers and Crop Production), and appropriate deductions for losses in storage and handling.

§ Gypsum, seaweed, peat moss, composts, wood ashes from home fires, phosphate rock applied as a separate material, sulfur, etc.

|| Preliminary.

TABLE 4

*Average regional application rates of MgO per acre of harvested cropland, by class of material,\* 1946*

REGION†	FERTILIZERS	LIMING MATERIALS	MANURES	MISCELLANEOUS	TOTAL
	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>	<i>pounds</i>
New England.....	4.6	28.5	7.8	.90	41.8
Middle Atlantic.....	3.4	24.3	8.0	.72	36.4
South Atlantic.....	8.2	20.4	4.8	.44	33.8
East North Central.....	0.69	43.8	6.0	.30	50.8
West North Central.....	0.04	13.9	4.6	.14	18.7
South Central.....	1.28	4.1	6.8	.20	12.4
Western.....	0.19	0.4	9.9	.34	10.8
United States.....	1.19	13.9	6.1	.29	21.5

\* See footnotes to table 3. The acreages of cropland used are preliminary figures from Agricultural Statistics 1946.

† For the states in a given region, see table 2.

liming materials supplied less than 100,000 tons of MgO to agriculture annually. This usage grew slowly until 1935, when it was 216,000 tons. The agricultural Conservation Program then caused it to grow rapidly. Liming materials supplied 2,405,311 tons of MgO in 1946. Thus this class, which in 1910 supplied less MgO than did fertilizers, contributed 12 times as much in 1946. Liming materials in 1946 provided 65 per cent of the total MgO applied to the soil, except in the form of crop residues, as compared with 16 per cent in 1935, and only 10 per cent in 1925. Similar percentages for MgO in fertilizers in 1946 and 1925 are 5.5 and 3.9, and for MgO in manures, 28 and 80.

Applications of MgO per acre of cropland are greater in the East North Central region than in any other, as shown in table 4. In this region most of the total MgO comes from liming materials. The Western region applies least MgO per acre of soil, and the bulk of it here is supplied by animal manures.

#### CONCLUSIONS

Fertilizers have always been a minor source of Mg for growing crops. In most years for the past century, fertilizers have contributed less than 6 per cent of the total added to the soil. Under most conditions the farmer can maintain both the Ca and Mg supply of his soil better and more economically by applying finely ground dolomitic limestone than by relying on fertilizer to supply it.

The average price in 1947 for ground limestone delivered to the farm in bulk ranged from \$2.50 per ton in Kansas for the high-calcic variety to \$7.50 in Florida for dolomite. The average cost was about \$3 a ton in most of the Central States, and \$4 to \$6 in the Atlantic Coastal States. In the form of fertilizer filler, dolomite costs the farmer at the rate of about \$16 a ton.

Where soils are deficient in Mg and it is not desirable to decrease acidity of the soil, or in areas where farmers habitually do not properly lime their land, it is better for manufacturers to add magnesian materials to commercial fertilizers. Such special conditions are believed to apply to the potato soils of the Northeastern States and to large areas of soils devoted to all crops in the Southeastern States.

#### SUMMARY

A brief history is outlined of the use of magnesium-containing materials in fertilizers.

The MgO contents of the various fertilizer materials and manures consumed in the United States in recent years are given. The average MgO contents are also shown for the liming materials consumed in most of the states.

From 1900 to 1933, total annual consumption of MgO in the form of fertilizers, manures, and soil amendments was close to 1,200,000 tons. In 1946, a peak consumption of 3,723,000 tons was reached. The rapid increase in recent years is due largely to an increased consumption of liming materials and a switch from high-calcic to dolomitic limestone. In 1910, liming materials supplied only 58,000 tons of MgO for agriculture as compared with 78,000 tons furnished by fertilizers, 933,000 tons by animal manures and 70,000 tons by miscellaneous

soil amendments, such as wood ashes, gypsum, and phosphate rock. Animal manures continue to supply about 1,000,000 tons annually, but this is less than one third of the total now, as compared with approximately eight tenths in years preceding 1934.

The average mixed fertilizer in 1910 contained 2.28 per cent MgO, and no material was added purposely to supply this nutrient. In 1944 and 1945, the average was 2.07 per cent MgO, over half of which was deliberately added in the form of magnesian materials. Dolomite supplies about six times as much MgO as all other magnesium carriers put together. Mixed fertilizers are frequently guaranteed to contain 2 or 3 per cent MgO when sold for potatoes in Maine and tobacco in North Carolina. The average present-day mixed fertilizer contains only about 0.3 per cent MgO when no dolomite or other special source of magnesium is included.

If no dolomite or magnesia had been used in 1944 to make mixed fertilizers, their physiological acidity would have been equivalent to 978,000 tons of calcium carbonate. The 496,000 tons of dolomite and 21,000 tons of other basic materials, mostly magnesia, reduced the acidity per ton from 230 pounds to 103 pounds. Thus the potential acidity of mixed fertilizers is now higher than it was on the average in 1937.

For many agricultural conditions, Mg can be obtained best in the form of ground dolomite applied directly to the soil. Under other conditions, Mg should be incorporated in the mixed fertilizers used. In most of the latter cases dolomite is the most economical source and is entirely satisfactory. Under some conditions water-soluble forms of Mg give best results.

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## BOOKS

*Fundamentals of Soil Mechanics.* By DONALD W. TAYLOR. John Wiley & Sons, Inc., New York, 1948. Pp. 700. Price \$6.

Although written for the benefit of graduate students in engineering, this book contains material that is highly interesting to those who are engaged in the study of soils in relation to agriculture. This is apparent from the chapter titles, which include: simple soil tests, soil classification, subsurface investigations, permeability, capillarity, seepage, shearing strength, stability of slopes, lateral pressures, soil mechanics, and considerations relative to dams. The book is well illustrated and it contains a considerable amount of very useful data. One of the most interesting figures is that showing the Casagrande soil classification for airfield projects. A set of problems is appended to each chapter, and a list of 174 references is given at the end of the book.

*The Home Owner's Guide to Better Lawns, Trees, and Gardens.* Edited by RICHARD B. FARNHAM AND VAN WIE INGHAM. Grosset & Dunlap, New York, 1948. Pp. 334, figs. 120. Price \$2.50.

This book was originally published under the title "Grounds for Living." It contains nine chapters: your home setting, lawn, shade trees, flowers, hobby crops, vegetables, fruits, soil, and outdoor construction. Each chapter is written by a specialist in the subject. The intent of the book is to meet the needs of the amateur in connection with the problems involved in yard and garden. It is nicely illustrated, and most of the chapters are followed by a list of well-chosen references for supplemental reading.

*Malabar Farm.* By LOUIS BROMFIELD. Harper and Brothers, New York, 1948. Pp. 405. Drawings by Kate Lord. Price \$3.75.

The sometimes peaceful but often very hectic life of an author-farmer, his family, the other families associated with the farming enterprise, a host of visitors, widely scattered friends the world over, and the farm animals, which "think they are people," are all subject matter for *Malabar Farm*. The book begins with a letter to a sergeant in Okinawa who has read "Pleasant Valley" and presumably is looking forward to a peaceful life on the farm when he comes back home. This is followed by extracts from *Malabar Journal*, chapters on such topics as the cycle of a farm pond, grass the great healer, some more animals, Malthus was right, the organic-chemical fertilizer feud, out of the earth we are born and to the earth we return, the bad year, and sportsmen's paradise. Hard fact, wholesome philosophy, and harmless fancy are interwoven so instructively and entertainingly that the reader is quite likely to stay up much later in the night than he had intended. The soil-plant scientist will be impressed with the intelligent approach of the author to the solution of the many problems that are faced by the farmer and that are associated with the agricultural enterprise, as it relates to the well-being of mankind.

*The Petrography and Petrology of South African Clays.* By V. L. BOSAZZA. Lund Humphries and Co. Ltd., London, 1948. Pp. 313, plates 17, figs. 15. Price 42/-.

This is a cloth-bound multigraphed issue of a thesis presented for the D.Sc. degree to the Natal University College, University of South Africa. It deals with the geochemistry of clays, size distribution of particles, their microscopic examination, mineral analysis, water and organic matter relationships, family groups, and the weathering, transportation, and sedimentation of rocks and their derivatives, with special reference to the clay fractions. The book contains many useful data and a very good bibliography of some 250 references. Anyone specially interested in clays or the clay fractions of soils will find this an interesting and useful addition to his library.

*Soil Physics.* Second Edition. By L. D. BAVER. John Wiley & Sons, Inc., New York, 1948. Pp. 398, figs. 89. Price \$4.75.

This book is probably the best in its field. The second edition is quite similar to the first in organization, the chapter titles being identical. The book deals primarily with the mechanical composition of soils, the characteristics of soil colloids, soil consistency, structure, water, air, and temperature, tillage, and runoff and erosion problems. The new material has to do with electron micrographs of clay particles, effect of microorganisms on soil structure, some thoughts on plowing, and the effects of rain on soil erosion. The lists of references that are appended to the several chapters have been lengthened considerably. The author is now director of the Hawaiian Sugar Planters' Association Experiment Station.

*The Squires Can Take It.* By LADD HAYSTEAD. Pelligrini and Cudahy, New York, 1948. Pp. 240. Price \$3.50.

City farmers have various motives in owning farms. These vary all the way from that of investment to that of having a place in which to bring up the children or merely to compete with other city farmers. As this book points out, some of these men are highly successful with their farming operations, and others, quite the contrary. Running through the critical examination into what these various types of city farmers are doing are a number of very important observations. Thus, the author writes of farm buildings: "Ignore the reproduction value of the buildings on any place you might buy. What you need are buildings for Tomorrow's farming—not Yesterday's horse-and-buggy days." The soil problem is analyzed as follows: "If there is a trend in this soil business it is toward giving more thought and doing less physical work on the substance that is the foundation of all life." Among the chapter headings are: hired hands you should know; don't romanticize—mechanize; structures are tools; goodbye, Mr. Weed; that vital partner (the wife); and city farmers and their clubs. Highly entertaining and illuminating, the book is the product of a good bit of very substantial thinking. Agronomists should read it.

*The Study of Plant Communities.* By HENRY J. OOSTING. W. H. Freeman and Co., New York, 1948. Pp. 389, figs. 190. Price \$4.50.

This introduction to plant ecology considers first the nature of the several plant communities and the methods by which they can be distinguished from one another. The factors that limit or modify these communities are then discussed. The methods of study employed in plant ecology are well presented. The illustrations are exceptionally good and well chosen. The last chapter is especially interesting in that it offers an applied ecological approach to the solution of the problems of soil conservation. A list of 276 cited references is appended. The book merits a wide reading and will be found very useful for reference purposes.

THE EDITORS.

#### INTERNATIONAL CONGRESS OF SOIL SCIENCE TO MEET

The Fourth International Congress of Soil Science will meet at Amsterdam, July 24 to August 1, 1950. Soil scientists interested in attending may obtain further information and a preliminary application form from the Secretary of the Organizing Committee of the Soil Science Congress, 3 Prof. van Hallstraat, Groningen, Netherlands.





## Dimitrii Nikolaevich Pryanishnikov 1865-1948

From Moscow on May 3, 1948, a news flash reported the death, at the age of 82, of Dimitrii Nikolaevich Pryanishnikov, who for 15 years was one of the consulting editors of SOIL SCIENCE.

Pryanishnikov was born November 7, 1865, in Kyakhata, Siberia, at the edge of the Gobi desert, a place of exile for revolutionists under the czars. His mother was the daughter of one of these revolutionists. His father, a native of Siberia, was a bookkeeper.

After graduating from a secondary classical school in Irkutsk, Siberia, Pryanishnikov entered the University of Moscow. Upon his graduation from the University, in 1887, he was offered the chair of general and organic chemistry. Instead, he chose to study agriculture, a choice prompted by his zeal for service to the Russian people, of whom at that time, more than 80 per cent were engaged in agriculture. He therefore entered the Petrovskaya Agricultural Academy, now known as the Timiryazev Academy. Here he studied plant physiology under Timiryazev, agricultural chemistry under Gustavson (known for his work on organic matter), and field crops under Stebut. In 1891, Pryanishnikov passed the examination for the master's degree and was appointed lecturer in agricultural chemistry, a post he held until 1929.

For 2 years, beginning in 1892, Pryanishnikov studied with Alfred Koch in Göttingen, with Duclaux at the Pasteur Institute in Paris, and in Schultze's laboratory in Zurich where he conducted research on the transformation of proteins in plants. Upon his return to Russia he continued his work on nitrogen metabolism, and between 1896 and 1900 he presented and defended his theses for the master's and the doctor's degrees. The title of his master's thesis was *The Decomposition of Proteins during Germination*, and that of the doctorate, *Proteins and their Decomposition in Relation to Respiration and Assimilation*. During this period he inaugurated at the Academy a course in the science of fertilizers and at the Moscow Agricultural Institute a series of lectures on field crops and on plant physiology.

In the 90's of the last century, an opinion prevailed among plant physiologists that protein decomposition in plant metabolism differs from that in animal metabolism. Pfeffer contended that asparagin in plants might be looked upon as a mobile form of nitrogen that, in translocation, differs from proteins as glucose differs from starch. Pryanishnikov showed that asparagin is merely a by-product of secondary synthesis of ammonia derived from oxidation of amino acids and from carbohydrate residues. In accord with Boussingault, Pryanishnikov held the view that the formation of asparagin in plants is physiologically similar to the formation of urea in the animal organism. His views were, at the time, hotly contested by Pfeffer and the rest of the German school of plant physiologists but were later corroborated by the successor of Pfeffer and by others.

A logical consequence of the work on asparagin was a study of the role of ammonia in plant nutrition. Pryanishnikov showed that the ammonia intake is related to the supply of carbohydrates, toxicity appearing when the supply of the latter is low. He demonstrated conclusively that ammonia is taken up by plants to good advantage and clarified the conditions under which this source of nitrogen is utilized.



DIMITRII NIKOLAEVICH PRYANISHNIKOV

Simultaneously with the nitrogen studies as the central theme, Pryanishnikov carried out a series of greenhouse and field experiments on the relation of other nutrients to nitrate and ammonia as sources of nitrogen. It is of interest to note that in his early studies Pryanishnikov predicted use in the near future of ammonium nitrate as a source of nitrogen in fertilizers. He lived to see his prediction fulfilled.

Another important contribution of Pryanishnikov, not so well known outside Russia, was his clarification of the problem of phosphate forms in fertilizer practices. As early as 1896 he differentiated the responses of the different zonal soil

types, specifically podzols and chernozems, to raw phosphate rock. In 1900 he noted the solubility effects of ammonia salts, especially ammonium sulfate, on rock phosphate. In 1903 he studied the effect of an excess of bases on phosphates in the soil and on the availability of iron and aluminum phosphates. Simultaneously he pointed out the acid-producing effects of ammonium sulfate and the necessity for liming when this salt is used as a source of nitrogen. He thus laid the theoretical and practical foundations for utilization of low-grade rock phosphates in combination with other salts. The successful developments in the Institute for Fertilizers in producing soluble phosphate from low-phosphorus-bearing rocks have been the logical results of Pryanishnikov's efforts for 10 years in this direction. More than 200 scientific papers on phosphorus in relation to the nutrition of plants and crop production appeared from his laboratory. Of these, more than 60 came from his pen.

The results of his work with raw phosphates as an adequate source of phosphorus in fertilizing the soil and the crop, he summarized as follows:

One must differentiate two groups of plants in their relation to phosphorus availability from rock phosphate. Some plants are capable of utilizing it independent of the reactions in the soil; other plants must depend on some reactions in the soil to get the phosphorus. By the same token, one must differentiate between the soils that are capable of enhancing the solubility of the phosphate and soils that are not capable of doing this. Thus, for the phosphate to be active it is essential to have either certain soil conditions or certain plant specifications.

Recognition of these facts has stimulated successful research in the direct utilization of rock phosphate.

Pryanishnikov was active in applying theory to practice. In this his extensive travels helped. He was among the early Russian students in *agro-chemistry* (the Russian designation for soil chemistry of the post-Liebig period) to appreciate the importance of adsorption of ions, exchange reactions, and buffer effects in the soil, though his bold beginnings have been overshadowed by the classical researches of Gedroiz. Pryanishnikov devoted a good share of his energies to developing crop rotation systems and soil management practices by the use of legumes, phosphates, farm manure, and by-products of industry, with very little use of the scarce<sup>1</sup> mineral salts of nitrogen and potassium.

On the subject of crop rotations, Pryanishnikov got into a controversy with the late R. R. Williams, one of the most colorful figures of Soviet agronomy,<sup>2</sup> whose ideas on systems of soil management were almost tantamount to the law of the country. Williams advocated a system of land management with grass culture for more than one year in the rotation. Pryanishnikov was for a system of crop rotation with phosphates and legumes as the key to soil productivity. Another point of difference between the two agronomists had to do with the effect of mineral fertilizer in plant-soil relationships. Pryanishnikov's view was

<sup>1</sup> Only in recent years have the potash works in Solikamsk and plants for fixation of nitrogen been developed in Russia.

<sup>2</sup> Williams was the son of an American engineer who was employed by the czarist government on railroad construction.

that the aim of fertilizer practices is to feed *the soil*, whereas the view of Williams was that the aim is to feed *the plant*. Williams detected in Pryanishnikov's approach to soil management and fertilization a departure from the philosophy of dialectics. This was a serious accusation, but Pryanishnikov stood his ground in the face of strong and powerful attacks. His pupils came to his rescue and defended him. With no casualties on either side, the flood of articles on this subject is the only record of the battle which lasted for several years, just prior to the outbreak of World War II.

Though neither Williams nor Pryanishnikov was of farm stock, very few men in Russia have done so much as they in determining the system of agriculture in the country. Their activities covered the field of agriculture from highly technical seminars and promulgation of research activities to the minute details of tilling and managing the soil and crops, type of plow, cultivator, or other implements used by the farmer in his daily work.

Pryanishnikov's manifold activities are reflected in the 17 volumes of *Iz Rezultatov Vegetatsionnykh Opytov i Laboratornykh Rabot* (Results of Vegetation Experiments and Laboratory work) published under his leadership and editorial supervision from 1894 to 1935. A wealth of information is stored in these volumes, and no small share of the contributions came from the editor himself. The topics discussed cover virtually all the ramifications of plant nutrition and soil science.

The western scientific world knows Pryanishnikov primarily as a plant physiologist. His classical researches on *Nitrogen in the Life of Plants and in Agriculture*, the title of his last monograph, published in 1945, are known throughout the world to students in the plant sciences and soil science. In Soviet Russia, Pryanishnikov is known as the agrochemist *par excellence*, the author of a series of papers and of a book on *Agrochemistry* which has gone through three editions, been translated into the Ukrainian, Armenian, Georgian, and Azerbaidzhan languages, and is now being translated into Bulgarian, English, and French.

Among his other books are: *The Chemistry of Plants: Part I—Carbohydrates*, and Part II—*Protein Substances; Fertilizers* (translated into Polish and German); *Chastmoe Zemledelie* (General Agriculture). The last is a comprehensive text of close to 800 pages which has been translated into German and several other languages and has gone through 10 editions, the last two under the title *Rasteniya Polevoi Kultury* (Field Crops) in collaboration with academician I. V. Yakushkin.

For his monograph on agrochemistry Pryanishnikov was awarded the "Stalin Prize of the First Order" and for his more than 400 scientific publications he received the most cherished honor of a Soviet citizen—"Hero of Socialist Labor."

Pryanishnikov's activity in the field of higher education might well form a chapter in itself. Prior to the Russian revolution, the scientist struggled with the authorities to maintain high standards in the Petrovskaya-Razumovskaya Academy. Under the czarist regime, the policy was to repress the number of students in the universities, and it was no easy task to battle with the bureaucratic officials of the government. Pryanishnikov attracted the better elements of the student body and induced them to get an all-round education. As a skill-



ful administrator, he knew how to engage the right kind of assistants and associates. The remarkable success he achieved in his researches was due largely to his sympathetic attitude and cooperative spirit. He was highly esteemed and loved by his collaborators, students, and disciples.

On the occasion of his 80th anniversary, appeared numerous papers honoring the "Dean of Russian Agriculturists, Academician Pryanishnikov." One item of the celebration was a list of 41 papers, which had been published over a period of years, devoted to the life and work of Pryanishnikov. Every paper stressed the role of Pryanishnikov as a scientist, a great teacher, an organizer of agricultural industry, and a practical agronomist.

J. S. JOFFE.



## Guy Wollard Conrey

### 1887-1948

Guy Wollard Conrey, professor emeritus of agronomy of the Ohio State University, died April 20, 1948, following a prolonged illness.

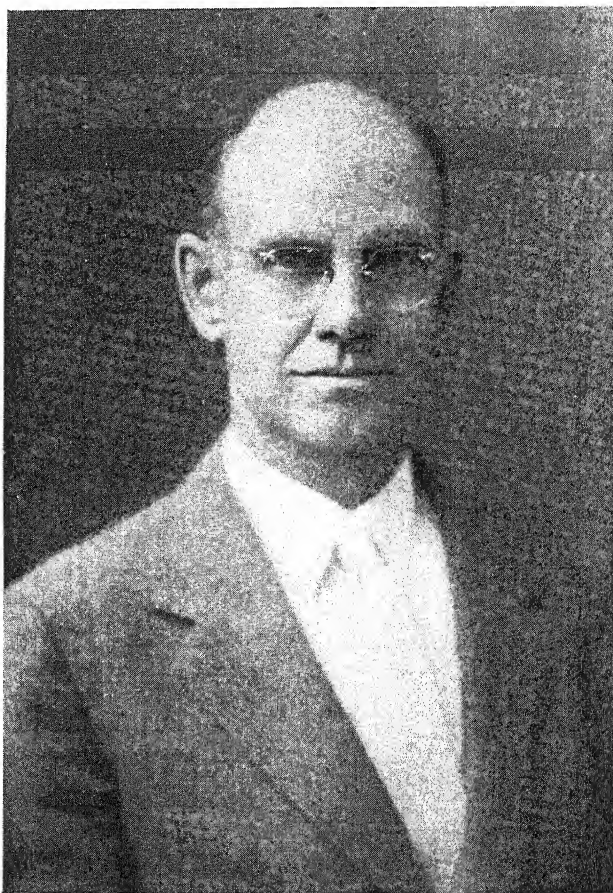
He was born at Northboro, Iowa, December 10, 1887. He received the B.A. degree in 1908 and the M.A. degree in 1909 from the University of Michigan, and the Ph.D. degree from the Ohio State University in 1921. From 1908 to 1921 he was assistant and instructor in physical chemistry and in soils from varying periods in Michigan and in Wisconsin. Following his appointment in 1917 as instructor in soils at Ohio State University and as assistant in soils at the experiment station, he held assistant, associate, and full professorships in agronomy at the university and was associate agronomist in charge of soil survey at the experiment station until his retirement on March 1, 1948.

Dr. Conrey was a fellow of the American Society of Agronomy and of the Ohio Academy of Science and a member of the American Association for the Advancement of Science, the American Geographic Association, the American Forestry Society, the Geophysical Union, the International Society of Soil Science, and the honorary societies of Sigma Xi, Phi Lambda Upsilon, and Gamma Sigma Delta. He served as president of the American Soil Survey Association in 1925, and after that organization merged with the Soil Science Society of America, he continued his activity with the new society, serving as chairman of Section I in 1943 and on several committees concerned with soil morphology, classification, technology, and soil physics.

Dr. Conrey's major agronomic interest was soil development and classification and land use. Working as a member of a relatively small group of pedologists, whose greatest contributions have come as a result of joint effort, he helped mold our present concepts of soil morphology and classification. More specifically, the careful laboratory and field examination of soils in Ohio by Dr. Conrey and his associates for the last 31 years has resulted in better understanding of practical agricultural problems, as well as of the more technical aspects of soil development and classification.

Dr. Conrey was an inspiring teacher. His deep understanding of soil science and its relationship to other sciences, together with his kindly nature and ability to explain complex relationships in simple language, endeared him to his students. His activity in the fields of geography, geology, and economics gave him a rare appreciation of the whole problem that was reflected in his teaching as well as in his research contributions.

In 1941, although his health was impaired, Dr. Conrey assumed extra duties directly concerned with the war. In addition to carrying his already heavy load of work, he taught courses in the A.S.T.P. and devoted his soils knowledge to helping locate airfield, manufacturing, and war materials storage sites. Doubtless, this great burden of work hastened the severe stroke he sustained in October,



GUY WOLLARD CONREY

1944, and from which he never fully recovered. During his last few years, though physically handicapped and confined to his home, he contributed a great deal to soil science through conferences, correspondence, and writings.

D. D. MASON.

# NITROGEN AND ORGANIC MATTER CONTENTS OF EQUATORIAL SOILS OF COLOMBIA, SOUTH AMERICA

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A number of years ago it was shown (14) that in the United States the nitrogen content and the organic matter content of the soil increase as the annual temperature decreases. The well-drained soils of southern states have a low average content of nitrogen, less than 0.05 per cent, whereas comparable soils of northern states have a high one, above 0.20 per cent. These relationships have been confirmed by Vanderford and Albrecht (26) and by Joffe and Conybeare (17).

Extrapolation of the North American nitrogen-temperature curves to the high annual temperatures prevailing in tropical regions leads one to expect that tropical soils are very low in nitrogen and organic matter. Confirmation of this belief was furnished by Mohr (20) who wrote: "In well aerated soils of the humid warm tropics with average temperatures over 25°C. (77°F.) humus cannot maintain itself, nor can it accumulate." Corbet (7), who investigated the soils of the Dutch East Indies, likewise stressed the low nitrogen content of tropical soils, but he offered a somewhat different explanation:

There appears to be no doubt that a further factor, that of insolation, is important in determining the nitrogen status of any given soil . . . high temperature unaccompanied by exposure to strong sunlight is of itself insufficient to produce the effects predicted by Jenny's law.

The first investigator who questioned the general validity of the American nitrogen-temperature relationships outside the United States was Dean (8). He reported the nitrogen content of 223 Hawaiian soil samples, having annual temperatures of 18–24°C. (65–75°F.) and an annual rainfall of 500–2,500 mm. (20–100 inches). Dean concluded:

It is clear that the nitrogen content of our soils does not agree at all with the data presented by Jenny. To be consistent, this [Hawaiian] average should be less than 0.1 per cent, whereas it is three times that. On the basis of soil nitrogen, Hawaii belongs just south of the Canadian boundary instead of south of the Tropic of Cancer.

Hardon's (11) analyses of the soils of primeval forests of southern Sumatra also indicate relatively high nitrogen levels. Ancizar-Sordo (4), in comparing the chemical compositions of Colombian soils with those of European soils, commented on the richness of the equatorial soils in total nitrogen.

<sup>1</sup> The senior author is indebted to the John Simon Guggenheim Memorial Foundation, and the Ministerio de Minas y Petroleos, Bogotá, for financial support, and to the Federación Nacional de Cafeteros de Colombia for providing living quarters in Chinchiná and assistance on expeditions. The author is especially grateful to J. Ancizar-Sordo and P. Schaufelberger for their stimulating interest and their realistic help in major issues as well as in the smallest details.



These conflicting reports are perplexing. Are the nitrogen-climate functions observed in the United States a strictly North American phenomenon, or do they have wider significance? To answer this question, the senior author spent half a year in the equatorial regions of Central and South America. In the present paper the results of a Colombian nitrogen survey are reported. A previous paper (16) gives detailed information on climate, soils, and sampling techniques.

#### ANALYTICAL TECHNIQUES AND COMPARATIVE ANALYSES

In Colombia, the senior author collected soil samples at about one hundred different localities. An attempt was made to obtain information on precipitation, temperature, vegetation, parent material, topography, drainage conditions, and cropping history, so that an interpretation of the nitrogen levels in accordance with the soil-forming factor equation (15) could be attempted.

After the soil samples had been passed through a 2-mm. sieve, they were divided into two parts. One was sent to the Laboratorio Químico Nacional de Analisis e Investigación (Dr. J. Ancizar-Sordo, Director) in Bogotá, Colombia; the other, to the soil chemistry laboratory at Berkeley, California.

About eighty samples were analyzed in both laboratories. At Bogotá total nitrogen was determined according to the Kjeldahl method (21) using selenium as a catalyst. At Berkeley the official A. O. A. C. method (5) was used. Copper and iron sulfates served as catalyst. Ammonia was distilled into boric acid and titrated with tenth-normal standard acid, using brom cresol green and methyl red as indicator. Total organic carbon was estimated according to Schollenberger's method (23) at Bogotá, but no correction factor was employed. At Berkeley, the dry combustion method was used (5). Each sample was ignited at a temperature of 900°C. for 75 minutes.

In figure 1 the nitrogen and carbon values obtained at Berkeley are plotted on the horizontal axis. The corresponding values obtained at Bogotá are marked off on the vertical axis. The Bogotá nitrogen figures tend to be slightly lower than the Berkeley analyses. This divergence might be the result of the different analytical techniques employed, or it might be the consequence of a more careful elimination of root fragments at Bogotá.

The discrepancy in the carbon analyses is especially marked. It reflects the difference in procedure, dry *versus* wet combustion. At Berkeley the correction factor was determined on 20 samples having a range in carbon content from 0.2 to 30 per cent. The Schollenberger method yielded, on the average, 86 per cent of the carbon values obtained by the combustion method. The extremes were 66 per cent and 100 per cent. On the right-hand graph of figure 1, the Bogotá carbon values cluster around the 0.86 line (broken) rather than the 1.00 line (solid).

These comparative results give a good general idea of the extent of agreement that might be obtained by different analysts using different methods in different laboratories.

At the Coffee Growers' Experiment Station in Chinchiná, humus is determined by ignition of an ammonium hydroxide extract of the soil (22). For 36 soils,

humus was determined at Chinchiná, and total nitrogen at Bogotá. The correlation existing between the two determinations may be expressed by the equation

$$H = 16.29N - 0.20$$

where  $H$  and  $N$  denote humus content and nitrogen content, both in per cent. The adjusted correlation coefficient is  $+0.95$ , and the adjusted standard error of estimate (10) is 0.93 per cent humus.

The hydrogen peroxide method was used<sup>2</sup> on a sample from a pasture in the vicinity of Albán near Bogotá. The loss in weight, which corresponds to the

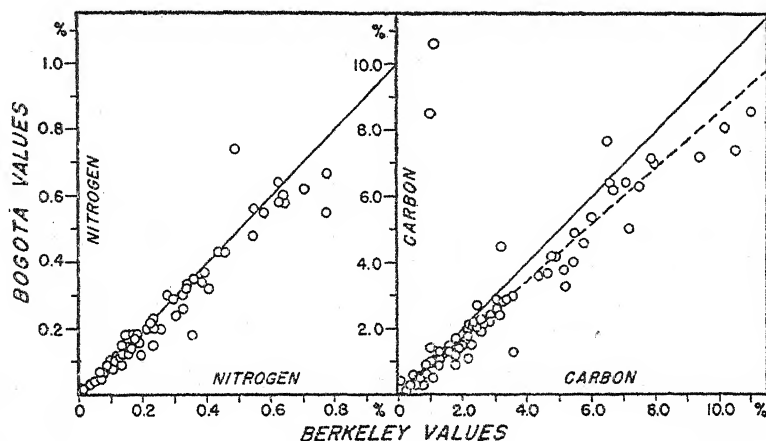


FIG. 1. COMPARISON OF NITROGEN AND CARBON ANALYSES OBTAINED AT BOGOTÁ AND BERKELEY

The solid lines indicate absolute equality (45-degree slope)

organic matter oxidized, was 19.22 per cent, expressed on an oven-dry basis. Dry combustion yielded a carbon content of 11.30 per cent, or 19.70 per cent organic matter, using the factor of 1.724. The agreement is satisfactory.

#### MOISTURE RELATIONSHIPS OF SOIL NITROGEN AND ORGANIC MATTER

Colombia offers unique climatic opportunities for the exploration of nitrogen-moisture functions at high temperatures. At low elevations having annual temperatures of 26–30°C. (79–86°F.) rainfall varies from 400–13,000 mm. (16–500 inches). In no other place in the Western Hemisphere do such extremes in precipitation occur. It is for this reason that Colombia was chosen as a place of investigation. The only drawback—and a greater one than originally anticipated—is the inaccessibility of many of the regions involved. Nevertheless, significant information could be obtained.

In figure 2 the annual precipitations are marked as abscissas, and the nitrogen contents of individual surface soils to a depth of 8 inches as ordinates. Forest

<sup>2</sup> By L. Rojas-Cruz, at Berkeley.

floors are excluded; only the mineral soils are considered. For each sample the organic carbon content also is indicated.

From the distribution pattern of the nitrogen values we may conclude that *nitrogen and organic matter increase as precipitation becomes higher*. The data, however, are too scanty and too variable to permit the formulation of a specific equation. Of special interest is the observation that in the hot humid tropics of Colombia the nitrogen and organic matter contents of virgin soils are high. To bring out more forcefully the general magnitude of the nitrogen levels, a dotted line designated as "U. S. A." indicates the nitrogen content that would be

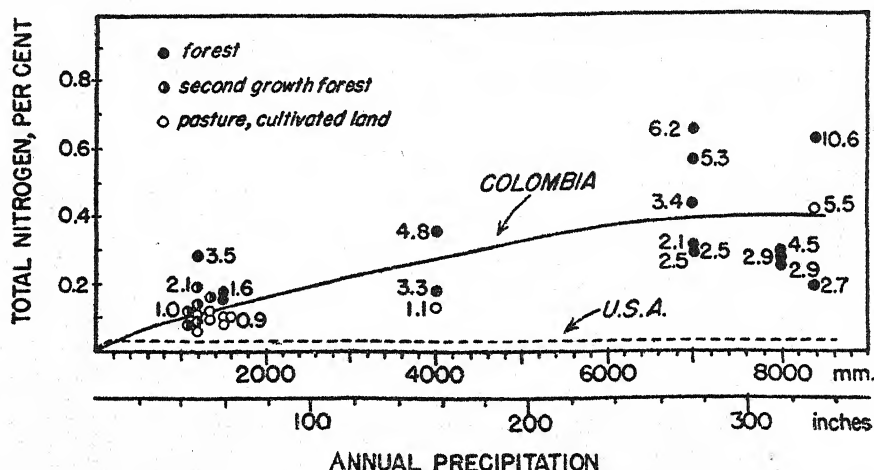


FIG. 2. NITROGEN-RAINFALL RELATIONSHIPS IN THE HOT ZONE OF COLOMBIA, S. A.

Mean annual temperature 26–30°C. (79–86°F.) Each dot represents one sample. The values listed adjacent to the dots indicate the organic carbon contents. The line "U. S. A." indicates the nitrogen content that would be expected if the nitrogen-temperature equations of the United States were extrapolated to Colombian environments.

expected if the nitrogen-temperature equations of the United States were extrapolated to Colombian environments. These values are much lower than those actually found. The tropical nitrogen levels are akin to those of the chernozem and prairie soils of the Red River Valley near the Canadian border.

Two significant conclusions may be drawn. First, extrapolation of the North American relationships between soil nitrogen and temperature leads to erroneous absolute values for Colombian tropical soils. Second, Mohr's much-quoted humus axiom (20) does not apply to the virgin and cultivated soils of Colombia.

#### ALTITUDE RELATIONSHIPS OF NITROGEN AND ORGANIC MATTER

In Colombia, altitude zonality of soils is outstanding. As one proceeds upward from sea level, the color of the soil becomes visibly darker, in accordance with its increasing content of organic matter. This altitude relationship is portrayed graphically in figure 3. Total nitrogen is plotted against elevation,

on the one hand, and against corresponding annual temperature, on the other (16).

Evidently the total nitrogen content of the surface soil (0-8 inches in depth) increases with rise in elevation. This observation agrees with the findings of Hardon (11) in Java, Dean (9) in Hawaii, Hockensmith and Tucker (12) in Colorado, and Sievers and Holtz (24) in Washington.

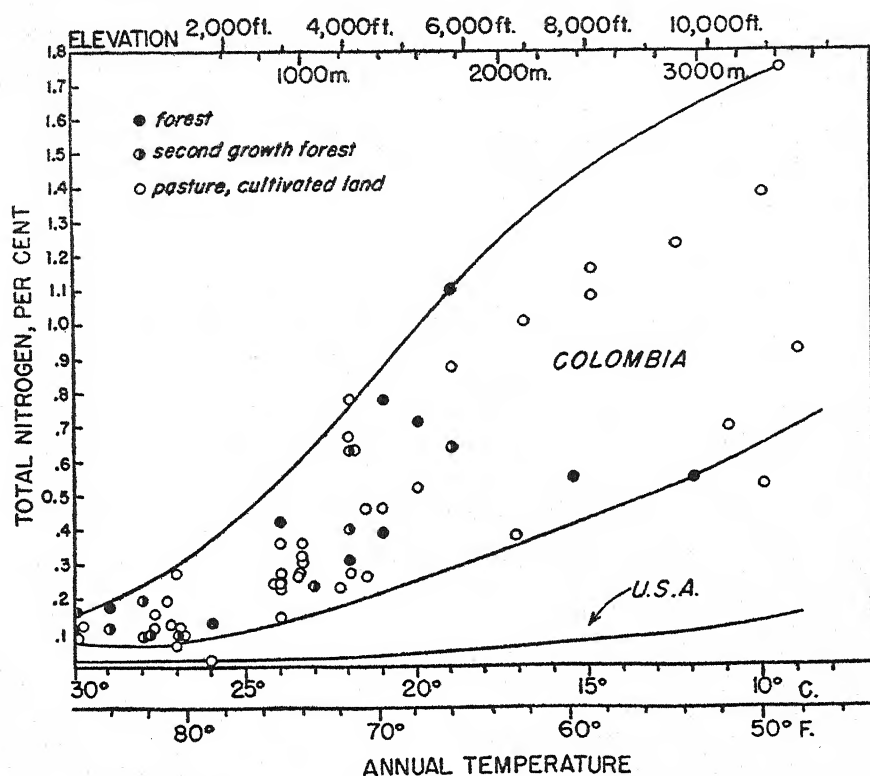


FIG. 3. RELATIONSHIP OF SOIL NITROGEN, ELEVATION, AND CORRESPONDING ANNUAL TEMPERATURE

Each point represents an individual sample. The curve "U. S. A." represents the nitrogen latitude function of the originally timbered soils of midwestern and eastern United States.

The scattering of the nitrogen values is considerable, as would be expected from the hurried selection of sites that had to be undertaken. Greater discrimination with regard to the soil-forming factors and the degree of erosion, especially at higher elevations, would in all likelihood furnish a family of well-defined nitrogen-altitude curves.

With mean annual temperature as a basis for comparison, the Colombian nitrogen-altitude correlation is related in figure 3 to a corresponding curve portraying the nitrogen-latitude function of the originally timbered soils of mid-



western and eastern United States (14). The high nitrogen levels of Colombian soils in contrast to those of the United States are strikingly brought out.

#### NITROGEN-CLIMATE FUNCTIONS

The rise of soil nitrogen with elevation is accompanied by variations in mean annual temperature and mean annual rainfall. An attempt was made to isolate the temperature variable for belts of constant rainfall and constant humidity factors (N. S. Q.). The following ranges of climatic moisture values were chosen:

##### *Mean annual rainfall belts*

- a) 900-1499 mm. (35-59 inches)
- b) 1500-2000 mm. (59-79 inches)

##### *Mean annual humidity belts*

- c) N. S. Q. 120-200
- d) N. S. Q. 201-400
- e) N. S. Q. 401-600

Dot diagrams indicated that within all five moisture belts the nitrogen content (N) of the soil to a depth of 8 inches could be related to mean annual temperature (T) by the simple exponential equation

$$N = k_1 e^{-k_2 T} \quad (1)$$

By multiplying both sides by 100 and then introducing Brigg's logarithms, equation (1) was converted to the straight-line equation

$$\log (100 N) = \log (100 k_1) - k_2 T \log e \quad (2)$$

For all five moisture belts the constants of equation (2) were determined by the method of least squares. By following the directions of Ezekiel (10) four statistical criteria were computed; namely,  $r$ ,  $\bar{r}$  coefficients of correlation, Fisher's  $t$ -value for  $r_1$ , and  $\bar{S}$ , standard error of estimate.

The constants of equations (1) and (2) and the statistical criteria are presented in table 1. Three of the scatter diagrams are shown in figure 4. The correlation coefficients for the five moisture zonations are statistically significant. It may be concluded, therefore, that *within constant moisture belts the nitrogen content of the soil increases exponentially as the mean annual temperature decreases through the interval 30° to 10°C.* This relationship is identical with that observed in the United States. The only difference lies in the magnitude of the constants. These are higher for Colombia than for the United States.

We may now derive nitrogen-moisture functions at constant temperatures by plotting, for example, the constants of  $k_1$  (5.90, 7.13, and 9.65) against the mid-points of the N. S. Q.-belts (160, 300, and 500). Since  $N = 0$  for N. S. Q. = 0, the nitrogen-N. S. Q. function may be described by the equation:

$$N = A [1 - e^{-k_3 \text{NSQ}}]_{T = 0^\circ \text{C.}} \quad (3)$$

The constants  $A$  and  $k_3$ , as determined by the trial and error method, assume the values of 12 and 0.0034, respectively. As may be recalled, equation (3) also obtains for the Great Plains area (14); however, the constants are different.



By combining equations (1) and (3), one obtains a nitrogen-climate surface for Colombian soils, having the form:

$$N = 12e^{-0.138T} [1 - e^{-0.0034 NSQ}] \quad (4)$$

The nitrogen content of the soil (0-8-inch depth) is related jointly to annual temperature ( $T$ ) and annual humidity (N. S. Q.). The experimental boundaries of the surface are given by the ranges  $T = 10-30^\circ\text{C.}$ , and N. S. Q. 120-500.

For the climatic ranges specified, two general features of the nitrogen-climate surface stand out:

a) At constant temperature, soil nitrogen increases logarithmically with increasing moisture.

b) At constant moisture, soil nitrogen declines exponentially as the temperature rises.

TABLE 1  
Constants of equations (1) and (2), and statistical criteria\*

CONSTANTS AND CRITERIA	RAINFALL 900-1499 MM.	RAINFALL 1500-2000 MM.	N. S. Q. 120-200	N. S. Q. 201-400	N. S. Q. 401-600
Number of samples.....	29	31	30	16	15
$k_1$ , equation (1).....	6.27	5.71	5.90	7.13	9.65
$k_2$ , equation (1).....	-0.140	-0.131	-0.138	-0.138	-0.138
$\bar{S}$ for equation (1).....	...	...	0.064	0.25 0.14†	0.21
$\log(100k_1)$ , equation (2).....	2.797	2.756	2.771	2.853	2.985
$k_2 \log e$ , equation (2).....	-0.061	-0.057	-0.060	-0.060	-0.060
$\bar{r}$ for equation (2).....	-0.837	-0.874	-0.592	-0.876	-0.577
$t$ -value for $r$ , equation (2).....	8.1	9.9	4.1	7.0	2.8
$\bar{S}$ for equation (2).....	0.184	0.180	0.167	0.133	0.195

\* Computed according to methods of Ezekiel (10).

† One low value of  $N$  omitted.

The shape of the Colombian nitrogen-climate surface is identical with the corresponding surface for the grassland soils of the Great Plains area (14, 15) which has the form:

$$N = 0.55e^{-0.087T} [1 - e^{-0.005 NSQ}] \quad (5)$$

In the two equations (4) and (5), only the constants differ, in accordance with the generally higher nitrogen levels of the soils of Colombia. In the light of this comparison, the following generalization is suggested: For a given pair of temperature and moisture values, the nitrogen content of the soil is much higher in Colombia than in the United States.

No claim is made that equation (4) gives the best statistical fit for the existing nitrogen values. Slightly differently shaped surfaces may describe the experimental data more accurately. The function will, however, as a first approximation, portray the distribution of existing soil nitrogen values in Colombia, as conditioned by mean annual temperature and mean annual N. S. Q.

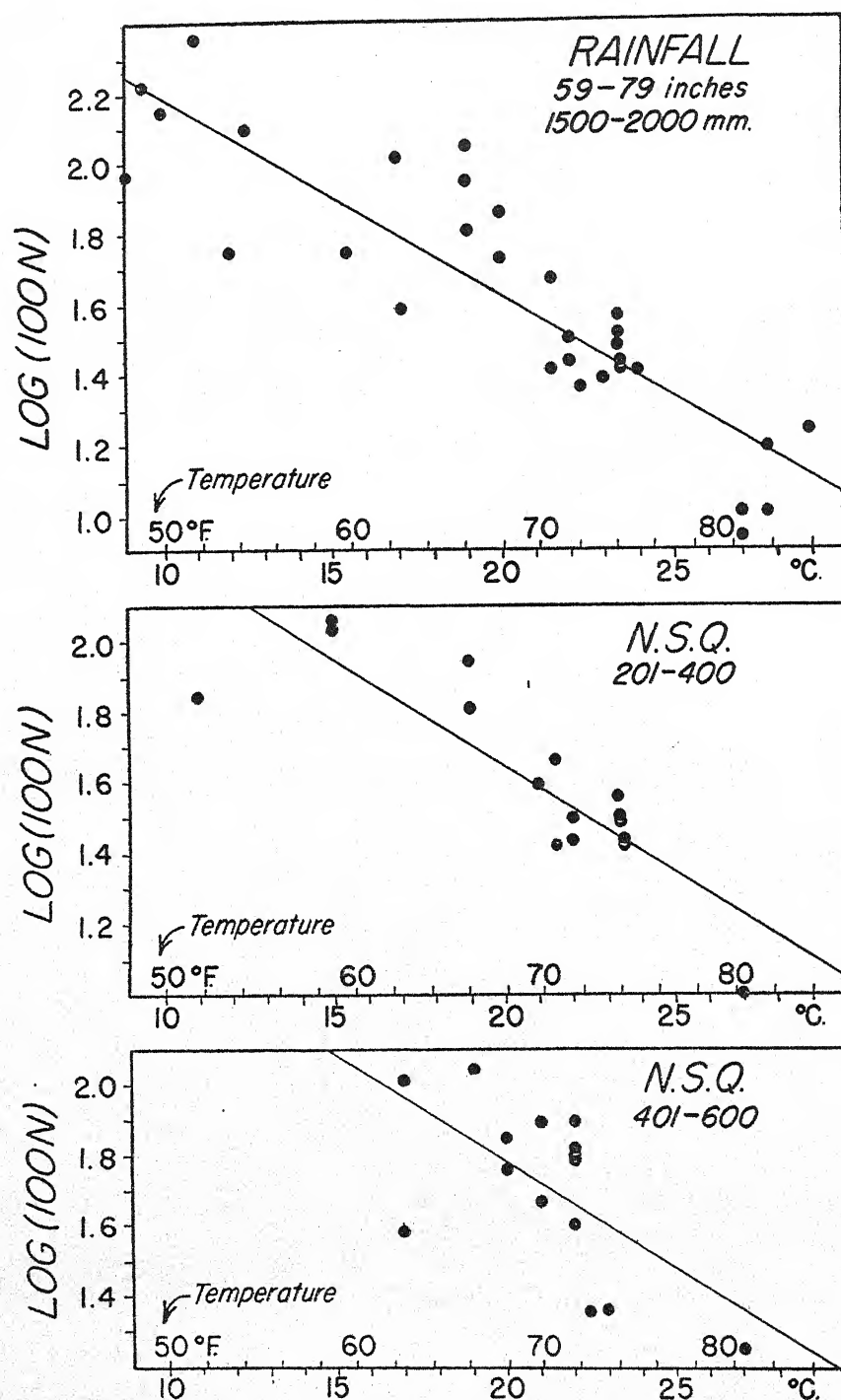


FIG. 4. NITROGEN-TEMPERATURE FUNCTIONS FOR BELTS OF CONSTANT MOISTURE  
 Lines drawn according to method of least squares

The statistical significance of the nitrogen-climate surface of Colombia may be appraised by the standard error of estimate. This is obtained by computing the standard deviation of the differences between the observed nitrogen values and the calculated nitrogen values. For the 61 nitrogen values used, the adjusted standard error of estimate ( $\bar{S}$ ) has a value of  $\pm 0.20$ . If one unusually low nitrogen value of 0.70 per cent N at  $T = 11$  and at N. S. Q. = 340 is excluded,  $\bar{S}$  has a value of  $\pm 0.15$ . It compares favorably with the  $\bar{S}$  values of the nitrogen-temperature functions [equation (1)] given in table 1.

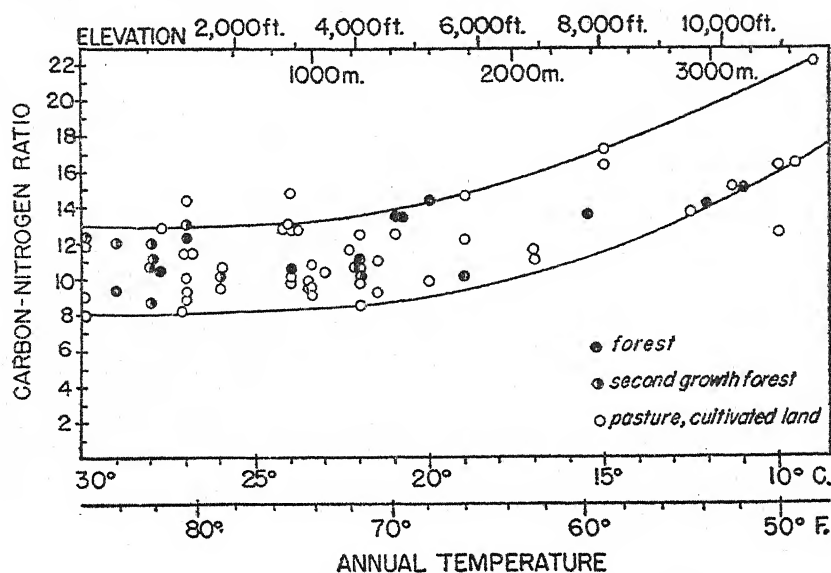


FIG. 5. CARBON-NITROGEN RATIOS OF COLOMBIAN SOILS IN RELATION TO ELEVATION AND CORRESPONDING ANNUAL TEMPERATURE

#### CARBON-NITROGEN RATIOS

In figure 5 are plotted the carbon-nitrogen ratios of the soil samples shown in the nitrogen-elevation graph of figure 3. The two lines enclose those soils which the author considers "normal" so far as the C/N quotient is concerned.

Assuming the validity of the two lines chosen, one may conclude that the carbon-nitrogen ratio increases with increasing elevation. This correlation confirms Hardon's observations in the primeval forests of Java (11). Hardon's graph is more conclusive because the scattering of his data is less pronounced.

In view of the systematic behavior of the carbon-nitrogen ratios in figure 5 it is evident that the nitrogen-climate functions, discussed in the preceding section, also reflect the variations of soil organic matter with climate.

#### RELATIONSHIPS BETWEEN SOIL COLOR AND SOIL NITROGEN

The senior author used to believe that he could estimate the approximate nitrogen content of the soil from its color in the field. In Colombia his guesses were

nearly always wrong. To evaluate the significance of this discrepancy on a quantitative basis, the color of all soils was determined according to the new color chart of the Division of Soil Survey, U. S. Department of Agriculture. In table 2, broad color groups are related to the nitrogen content of the soil. The four groups selected comprise the following specific colors:

<i>Color group</i>	<i>Specific colors</i>
Yellow:	Yellow, pale yellow, brownish yellow, reddish yellow.
Light brown:	Very pale brown, pale brown, light yellowish brown, yellowish brown.
Brown and grayish brown:	Brown, grayish brown, dark grayish brown.
Gray:	Light gray, light brownish gray, gray, dark gray.

While no close relationship exists between soil color and nitrogen content, except for the color extremes such as yellow versus dark grayish brown, two

TABLE 2  
*Color and nitrogen content of soils and subsoils*  
Figures indicate number of soil samples in each nitrogen class

NITROGEN CLASSES	COLOR GROUPS			
	Yellow	Light brown	Brown and grayish brown	Gray
<i>per cent</i>				
<0.09	17	13	5	2
0.10-0.19	9	10	14	5
0.20-0.29	4	4	8	3
0.30-0.39	...	7	8	...
0.40-0.49	1	2	6	1
0.50-0.59	...	...	4	...
0.60-0.69	...	...	5	...
0.70-0.79	...	1	4	...
>0.80	...	1	5	1

surprising features deserve comment. First, a considerable number of yellow and light brown soils are unusually rich in organic matter. They contain more than 0.20 per cent nitrogen. Vageler's (16) assertion that tropical humus substances are colorless seems to contain an element of truth. Second, the brown and grayish brown soils vary tremendously in their nitrogen content. Of 22 brown soils, 11 contain more than 0.30 per cent nitrogen. Of 21 dark grayish brown soils, 11 exceed the limit of 0.50 per cent.

Although no similar study exists for North American soils, it is probably safe to surmise that in a comparison of soils of equal color, those from Colombia tend to be higher in nitrogen and organic matter than those from the United States.

#### AMOUNT AND NATURE OF FOREST FLOOR MATERIAL

A square metal frame having sharpened lower edges and an inside, open area of 584 sq. cm. was firmly pressed into the ground. The tool neatly cut all the leaves and woody parts of the forest floor. The organic material inside the

frame and above the mineral soil was gathered and put into light cloth bags. In the laboratory the samples were dried at 60°C. Leaves and woody parts were separated and weighed individually in air-dry condition. Roots were

TABLE 3  
Weight and composition of forest floor samples  
Oven-dry basis

SAMPLE NUMBER	WEIGHT OF SAMPLE		WOOD	TOTAL NITROGEN				ORGANIC CARBON			pH	
				In wood	In leaves	Total floor	In soil 0-8 inches	In wood	In leaves	Total floor	Wood	Leaves
	gm./sq.m.	lbs./A.	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent		
Region of Calima and Villavicencio (No. 97); hot, perhumid climate												
75	284	2533	8.2	...	1.41	...	0.28	...	47.01	...	...	5.4
76	504	4496	0	...	1.75	1.75	0.62	...	43.19	43.19	...	4.7
80	697	6217	43.4	0.92	2.36	1.64	0.25	48.02	43.68	45.85	5.0	4.5
81	336	2997	50.6	0.80	...	...	0.27	37.90	...	...	5.7	...
97	633	5646	4.3	...	...	1.32	0.18	...	...	39.67	4.4†	...
Av.	491	4378	...	0.86	1.84	1.57	...	42.96	44.62	42.90	...	...
Magdalena Valley (Tolima, Huila); hot, semihumid to semiarid climate												
49	1454	12970	49.2	0.71	2.54	1.64	0.15	39.30	38.09	38.69	5.9	6.7
51	660	5887	59.7	1.54	2.31	1.85	0.17	43.62	34.54	39.96	6.2	6.8
53*	920	8206	15.8	0.71	1.34	1.24	0.12	46.91	41.20	42.10	6.1	6.2
54	953	8501	29.8	1.06	1.33	1.26	0.08	41.16	38.44	39.25	6.3	6.4
56	724	6458	44.5	1.00	1.60	1.33	0.19	40.17	40.75	40.50	6.4	6.8
59*	700	6244	75.1	0.84	2.16	1.17	0.16	44.96	43.01	44.47	6.1	...
60	1377	12280	37.0	0.49	1.77	1.30	0.11	49.09	41.06	44.03	6.2	6.7
63	1303	11623	13.6	0.63	0.67	0.67	0.14	45.39	44.21	44.37	...	5.9
64	1259	11230	20.0	0.81	1.41	1.29	0.28	45.79	37.36	39.05	6.2	6.8
Av.	1039	9267	...	0.87	1.68	1.31	...	44.04	39.85	41.38	...	...
State of Caldas; subtropical-temperate, humid climate												
26½	1153	10285	24.2	...	...	0.89	0.31	...	...	44.45	5.5†	...
39*	734	6547	5.5	...	...	1.65	0.53	...	...	36.71	5.8†	...
40	1072	9562	2.0	...	...	1.37	0.63	...	...	34.75	6.5†	...
73	1648	14700	32.8	1.36	1.46	1.43	0.78	49.33	47.56	48.19	5.0	6.0
Av.	1152	10274	...	...	...	1.34	...	...	...	41.03	...	...

\* Cut-over forests; all others are virgin or nearly virgin forests.

† pH of composite.

eliminated as far as possible. Leaves and wood were then passed through a Wiley mill. Moisture was determined on aliquot parts at 105°C. The moisture content of the air-dry, ground material varied from 7-15 per cent (average 12.09 per cent).

As shown in table 3, the forest floors from the yellow soils of the hot, perhumid rain forest were found to weigh the least. Indeed, in these regions the soils are



only partly covered with leaves and twigs. In contrast, in the subtropic and temperate region of Caldas, where the humic yellow-brown soils occur, the soils are covered with forest floors several inches thick.

The samples from the tropic gray-brown soils of the Magdalena Valley may not be wholly representative of normal conditions. According to statements by local residents, the authors' field trips occurred at the end of a dry season, which might have caused an above-average leaf fall. As a matter of fact, all samples from the Magdalena Valley contain a relatively high portion of undecomposed leaves. As soon as the meteorological records of Girardot, Espinal, and Nieva for the fall of 1946 become available, this irregularity may be evaluated.

A comparison with conditions in the United States (table 4) reveals that the weights of the Colombian forest floors are of similar magnitude to those from

TABLE 4  
*Weights of forest floors in the United States*  
(Mostly on oven-dry basis)

LOCALITY	VEGETATION	NUMBER OF SAMPLES	WEIGHTS IN POUNDS PER ACRE		AUTHOR
			Range	Average	
Minnesota and Wisconsin	Basswood, maple, aspen, birch	16	25,050*-59,787	39,556	Alway <i>et al.</i> (1, 2, 3)
Connecticut	Hardwoods	5	7,000-94,000	60,244	Lunt (19)
Fern Canyon (California)	Chaparral	101	10,000-47,000	33,200	Kittredge (18)
Ohio, Indiana	Sassafras, black locust	?	6,800-10,200	8,500	Auten (6)
Ashville (North Carolina)	Pine-oak	2	6,300-7,900	7,100	Sims (25)
South Appalachians	Hardwood	5	3,146-16,359	10,435	Hursh (13)

\* One low sample (8,340 pounds) omitted.

the midwest and southern states. The total nitrogen contents of the Colombian samples correspond to those reported by Alway (3) for the northern hardwoods.

Conceivably, a proportionality might exist between the magnitude of the forest floor and the organic matter content of the surface portion of the mineral soil. In table 3 are listed the total nitrogen contents, to a depth of 8 inches, of those mineral soils from which the forest floors were collected.

The expected dependency exists for the average of the hot, perhumid Calima soils as contrasted with the average of the Caldas soils. The Magdalena Valley soils constitute an exception. Despite high forest-floor values, the nitrogen contents of the mineral soils are relatively low.

An unusual sample from the hot, perhumid zone of Calima is excluded from table 3. It belongs to the yellow podzolic soils which occur on a slightly elevated plateau in the region of the tropic yellow-brown soils. The forest floor consists of a 1-inch layer of slightly decayed leaves and twigs containing 17.0 per cent woody parts and weighing 6,226 pounds per acre. Analyses revealed the following com-

position: N = 0.89 per cent, C = 48.28 per cent, pH = 5.2. This leaf cover is underlain by a 4-inch layer of well-decomposed leaves weighing 13,630 pounds per acre. The composition of this lower layer is as follows: N = 1.59 per cent, C = 47.50 per cent, pH = 4.0. As indicated previously (16), it is not clear why such a thick layer of raw humus should exist within the zone of yellow soils which have a relatively low humus content.

#### SUMMARY

Soil samples were collected in about 100 different localities in Colombia, S. A. Nitrogen and carbon determinations were made at Bogotá, Colombia, and at Berkeley, California. The agreements are satisfactory.

At high annual temperatures—as they prevail at low elevation—nitrogen and organic matter increase as precipitation becomes higher.

As one climbs from sea level to high altitudes, a marked increase in soil nitrogen and organic matter becomes noticeable.

For belts of constant rainfall and N. S. Q. the nitrogen content increases exponentially as the temperature decreases.

A nitrogen-climate surface may be constructed for Colombian soils which has the same shape as the nitrogen-climate surface for the soils of the Great Plains area. However, the magnitudes of the constants in the two equations differ.

In a comparison of Colombian and North American soils having equal annual temperatures and annual moisture values, it is found that the Colombian soils have much higher nitrogen and organic matter contents than the North American soils.

Many light colored soils from the hot and humid areas are rich in nitrogen and organic matter.

The weight of forest floor per unit area is low in the primeval forests of the humid hot zones. In the subtropical and temperate regions it is higher and corresponds to that of the central United States.

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# MOLYBDENUM CONTENT OF PASTURE PLANTS IN RELATION TO TOXICITY TO CATTLE

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For many years cattle grazing in certain districts of the San Joaquin Valley, California, have been affected with a peculiar disease for which no pathological organism has been found. The symptoms of the disease are severe diarrhea followed by roughening of the coat, change of color, and loss in weight. In severe cases the hair sheds in spots leaving reddened, dry, and cracked skin. Young animals are most severely affected, and they often show stiffness in the hind legs. In some instances dairy cows have been found difficult to breed and, if they become pregnant, are likely to abort. Death of the animals has resulted in a number of cases. The symptoms of the disease are similar to those of a disease in cattle reported from certain parts of England, the cause of which was discovered to be excessive Mo in the pasture plants (7).

Britton and Goss (5) presented preliminary evidence that Mo may be the cause of the disease in California. To explore this hypothesis more thoroughly, Mo has been determined in the soil and pasture plants from many ranches where the cattle were affected and also from areas where the animals were unaffected.

Molybdenum was determined by the stannous-chloride-thiocyanate method as modified by Barshad (3). The plants were collected at random from a given field and analyzed in duplicate. A special study was made on the distribution of Mo in plant parts. This, it was thought, would be of particular interest since it is only in recent years that Mo has been considered an essential element for plant growth (2). It is well known that the nitrogen-fixing bacteria require Mo (1, 4, 6, 8).

## MOLYBDENUM CONTENT OF SOILS

As is shown in table 1, the total Mo of the soils where cattle are affected is not high. It ranges from 1.5 to 10.0 p.p.m., a high percentage of which is soluble in water. It was found that the high solubility of Mo in these soils is due mainly to their alkaline reaction, for by acidification, water-soluble Mo was greatly reduced. The Mo is present in the largest amounts in the surface foot of soil. In the soil with the highest amounts it ranges from 10 p.p.m. in the surface foot to 5 p.p.m. in the fifth foot below the surface, and in the soil with the smallest amounts it ranges from 1.5 p.p.m. in the surface foot to 0.8 p.p.m. in the fifth foot below the surface.

Among the unaffected areas reported in table 1, the Mo content of the soil was found to range from a trace to 0.5 p.p.m. Other unaffected areas in Southern



California have been found by Vanslow<sup>1</sup> to contain 3 to 4 p.p.m. Table 2 shows the Mo content of a number of California soils.

TABLE 1  
Average molybdenum content of plants (leaves and stems) as related to molybdenum content of soils

Mo, in p.p.m. dry matter

MOLYBDENUM CONTENT OF total* SURFACE FOOT OF SOIL (soluble† at pH 8. ....	10-5‡ 6-3	4-1.5‡ 2-0.8	0.5-trace§ trace
Molybdenum content of plant			
<i>Vicia americana</i> .....	220	...	...
<i>Medicago hispida</i> .....	200-100	54-36	8-0.8
<i>Lotus corniculatus</i> .....	150- 40	47-16	11-4
<i>Trifolium repens</i> .....	150- 80	50-12	5-3
<i>Trifolium fragiferum</i> .....	...	50-12	5-4
<i>Trifolium subterraneum</i> .....	175- 50	...	...
<i>Melilotus alba</i> .....	80- 30	77-18	22-5
<i>Melilotus officinalis</i> .....	80- 28	55-14	5-2
<i>Melilotus indica</i> .....	80- 50	30-15	13-7
<i>Medicago sativa</i> .....	30- 15	16-13	5-1.3
<i>Triticum vulgare</i> .....	27	...	...
<i>Avena sativa</i> .....	21- 5	7-6	4-2
<i>Hordeum vulgare</i> .....	18- 17	...	...
<i>Chloris gayana</i> .....	40- 14	13- 5	...
<i>Lolium perenne</i> .....	33- 10	18- 7	4-2
<i>Festuca elatior</i> .....	...	7- 2	...
<i>Dactylis glomerata</i> .....	...	9- 5	...
<i>Paspalum dilatatum</i> .....	9- 2	4- 2	...
<i>Sorghum vulgare sudanese</i> .....	7- 2	...	...
<i>Cynodon dactylon</i> .....	11- 3	7- 4	...
<i>Sorghum halepense</i> .....	5	...	...
<i>Erodium cicutarium</i> .....	...	13- 2	...

\* By fusion with Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>.

† In water, 0.1 N NaOH, 0.1 N (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, or 0.2 N (NH<sub>4</sub>)<sub>2</sub> tartarate.

‡ If legumes comprised a substantial percentage of the pasture plants on these soils, cattle were severely affected. Where grasses, with the exception of Rhodes and rye grass, constituted the only plants in the pasture, cattle were not adversely affected.

§ Cattle normal.

#### MOLYBDENUM CONTENT OF PLANTS

As shown in table 1, legumes tend to absorb considerably larger amounts of Mo than do nonlegumes, particularly when grown on soils with high soluble Mo. Certain legume species apparently absorb increasing amounts of Mo as the soluble Mo increases, while others do not show this relationship. The Mo content of certain species of nonlegumes was roughly correlated with that of the soil, but this correlation was not well marked with other species. On soil high in soluble Mo, large differences in the Mo content of the plant were found among different varieties of the same species when grown in the same pot and harvested at the same time, as shown in table 3.

<sup>1</sup> Unpublished.



TABLE 2  
*Total molybdenum in some California soils*

SOIL	LOCATION	COUNTY	DEPTH	Mo	pH
			<i>inches</i>	<i>p.p.m.*</i>	
Merced clay loam	Coloma	Kern	0-12	9.7	7.3
			12-24	5.8	7.9
			78-84	5.0	7.5
Merced clay loam	Buttonwillow	Kern	0-12	6.8	7.3
			36-48	5.8	8.7
			48-60	3.0	9.1
Merced clay loam	San Joaquin	Fresno	0-12	7.0	7.6
			24-36	2.5	8.1
Merced clay loam	Helm	Fresno	0-12	2.9	7.5
			12-24	2.5	7.2
			36-48	1.3	6.8
Foster sandy loam	Greenfield	Kern	0-12	3.3	7.3
			12-24	2.6	7.9
			24-36	2.1	7.4
			48-60	1.8	8.1
Foster sandy loam	Helm	Fresno	0-12	2.1	8.4
			24-36	2.1	9.7
Foster sandy loam	Helm	Fresno	0-12	1.5	7.9
			36-48	0.8	9.3
Hesperia sandy loam	Wasco	Kern	0-12	1.5	7.9
			60-72	2.1	9.4
Hesperia sandy loam	Shafter	Kern	0-12	1.6	7.3
Panoche clay loam	Los Banos	Merced	0-12	0.8	7.6
Hanford sandy loam	Lodi	San Joaquin	0- 6	0.3	7.0
Yolo silt loam	Davis	Yolo	0- 6	0.1	7.3
Yolo clay loam	Davis	Yolo	0- 6	0.4	7.6
Los Osos clay loam	Danville	Contra Costa	0- 6	0.1	6.1
Colma sandy loam	Colma	San Mateo	0- 6	0.1	7.1
Cayucos clay loam	Rodeo	Contra Costa	0- 6	1.0	5.7
Gleason clay loam	Alturas	Modoc	0- 6	0.1	6.8
Sheridan clay loam	Montara	San Mateo	0- 6	0.2	6.4
			24-30	0.4	6.7
Holland loamy sand	Mt. Oreum School	El Dorado	0-16	0.5	5.6
			37-56	0.7	5.5
Sierra sandy loam	Mt. Oreum	El Dorado	0- 8	0.2	5.6
			33-43	0.4	5.2

\* Air-dry soil.

Table 4 shows the effect of stage of development on the Mo content of several species of plants. All of them, whether high or low in Mo, showed twofold to threefold increases in Mo from spring to fall.

TABLE 3  
*Molybdenum content of two varieties of Lotus corniculatus grown in the same pot*

VARIETY	Mo IN LEAVES		
	Sample 1	Sample 2	Sample 3
	p.p.m.	p.p.m.	p.p.m.
<i>vulgaris</i> .....	202	110	38
<i>tenuifolius</i> .....	55	33	4.5

TABLE 4  
*Effect of season on molybdenum content of plants (leaves and stems)*

PLANT	LOCATION*	Mo CONTENT OF PLANTS†		
		Spring— April and May	Summer— June and July	Fall—Sep- tember and October
		p.p.m.	p.p.m.	p.p.m.
Alfalfa.....	Coloma	16.0	20.0	28.4
Alfalfa.....	Buttonwillow	9.2	11.3	18.0
Alfalfa.....	Greenfield	10.4	13.6	16.2
Alfalfa.....	Pond	5.2	7.5	12.9
<i>Melilotus alba</i> .....	Pond	...	32.0	77.5
<i>Melilotus alba</i> .....	Greenfield	18.1	44.8	...
<i>Lotus corniculatus</i> .....	Greenfield	30.0	43.6	92.9
<i>Lotus corniculatus</i> .....	Wasco	20.6	31.0	72.0
<i>Lotus corniculatus</i> .....	Buttonwillow	...	54.6	86.8
Rhodes grass.....	Buttonwillow	8.1	14.0	25.0
Rye grass.....	Greenfield	2.5	4.3	6.5
Rye grass.....	Shafter	4.3	7.5	10.0
Rye grass.....	Buttonwillow	...	22.3	33.5
Orchard grass.....	Pond	1.7	5.0	...
Orchard grass.....	Shafter	3.6	4.9	9.8
Orchard grass.....	Wasco	4.7	...	8.5
Water grass.....	Buttonwillow	3.9	...	8.2
Bermuda grass.....	Greenfield	4.0	...	7.6

\* All places listed are in Kern County.

† Dry-matter.

Table 5 shows Mo content of the leaves of Ladino clover, *Lotus corniculatus*, and Rhodes grass at various ages when grown in pot cultures in soil high in soluble Mo (6-3 p.p.m.). The data show that, with each species, Mo continued to accumulate in the leaves as the plants grew older. The data also show a wide difference between legumes and a nonlegume.

Ter Meulen and Ravenswaay (10) found that the leaves of deciduous trees growing in Holland varied in Mo content with age but much less markedly than the plants used in the pot cultures. Furthermore, none of the deciduous leaves was found to contain more than 0.58 p.p.m. Mo.

Table 6 shows the distribution of Mo in plant parts of several samples of various species grown on various soils and collected at various times. In general, the Mo content was greatest in those parts of the plant which have a high metabolic activity, such as leaves, growing points, runners, and nodules. On the other hand, the Mo content was lowest in plant parts with low metabolic activities, like old stems and old roots. The Mo content of the reproductive plant parts was found to be intermediate between that of the most active and the least active parts.

TABLE 5  
*Molybdenum content of leaves in relation to age*  
Mo, in p.p.m. dry matter

AGE, DAYS FROM GERMINATION.....	21	28	44	66	96	140
	Mo content of leaves					
Ladino clover.....	63	...	100	123	...	...
Ladino clover.....	50	...	56	96	...	...
Ladino clover.....	...	12	...	31	...	...
<i>Lotus corniculatus</i> .....	51	...	77	156	...	...
<i>Lotus corniculatus</i> .....	49	...	53	131	...	...
<i>Lotus corniculatus</i> .....	...	12	...	19	...	...
Rhodes grass.....	...	8	...	17	45	55
Rhodes grass.....	...	9	...	18	23	41
Rhodes grass.....	...	10	...	15	27	37

#### EFFECT OF MOLYBDENUM APPLICATION

Ammonium molybdate was applied, at the rate of 10 and 50 p.p.m. of Mo, to Aiken clay loam with a low molybdenum content (0.3 p.p.m.). *Lotus corniculatus* var. *vulgaris* was then grown in pots each containing 1,600 gm. of soil. The yield and the molybdenum content of the leaves and stems of the first and second cuttings are reported in table 7. The added molybdenum had no effect on the appearance or the yield of the plants, but the Mo content of the plants was increased in direct proportion to the molybdenum applied. These results bear out the field observations that the molybdenum content of certain species is related to the Mo content of the soil and that Mo in the plant may vary widely without any deleterious effect on the plant.

#### RELATION OF MOLYBDENUM CONTENT OF PLANTS AND INJURY TO CATTLE

The results reported in table 1 show that, in general, wherever the abnormality of cattle referred to herein has been found, a large proportion of the pasture

TABLE 6  
Molybdenum content of different parts of plants  
Mo, in p.p.m. dry matter

PLANT	PLANT PART	Mo CONTENT					
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Alfalfa	Leaves	2.1	...	6.4	13.1	15.8	23.5
	Stems	0.8	9.4	2.6	6.0	6.1	8.9
	Flowers	1.6	...	...	...	...	...
	Roots	...	11.3	...	...	...	...
<i>Melilotus alba</i>	Leaves	18.9	23.2	23.5	87.3	...	...
	Thin stems	35.0	...	28.0	67.2	...	...
	Thick stems	...	12.4	6.5	30.2	...	...
<i>Melilotus officinalis</i>	Leaves	7.2	18.3	62.5	48.4	...	...
	Thin stems	9.1	..	...	48.0	...	...
	Medium stems	4.8	8.0	33.7	...	...	...
	Thick stems	1.9	...	...	37.3	...	...
Burr clover	Leaves	9.7	23.0	36.5	309.2	...	...
	Stems	27.0	65.2	92.7	408.0	...	...
	Burrs	11.4	30.7	37.1	114.1	...	...
Subterranean clover	Blades	72.0	22.7	98.1	200	29.8	59.9
	Petioles	50.8	30.8	58.2	96	40.4	85.1
	Growing point	64.4	47.6	...	...	...	...
	Runner	160.0	...	...	...	...	...
	Nodules	53.4	...	...	...	...	...
	Roots without nodules	8.8	...	...	...	...	...
Ladino clover	Blades	32.2	68.5	65.2	32.3	44.4	201.0
	Petioles	29.9	54.4	59.0	31.8	15.5	73.1
	Runner	74.5	97.6	...	...	...	...
	Nodules	119.5	77.0	...	...	...	...
	Roots without nodules	16.5	36.3	...	...	...	...
	Rootlets with nodules	...	...	134.1	81.0	...	...
	Seed	...	...	...	...	20.0	...
<i>Lotus corniculatus</i>	Leaves	5.2	103.8	133.0	17.5	28.3	202.0
	Stems	9.8	84.0	100.4	30.3	33.2	63.0
	Flowers	4.4	...	58.7	...	...	...
	Pods	5.1	48.8	...	...	...	...
	Nodules	...	...	...	25.0	28.8	...
	Roots without nodules	...	...	...	28.7	15.9	...
Barley	Stems	12.9	...	...	...	...	...
	Grain	5.4	...	...	...	...	...
Oats	Stems	3.6	...	...	...	...	...
	Grain	2.0	...	...	...	...	...
Rye grass	Blades	33.5	...	...	...	...	...
	Stems	19.0	...	...	...	...	...
	Beards	13.6	...	...	...	...	...
Rhodes grass	Blades	28.4	...	...	...	...	...
	Stems	25.3	...	...	...	...	...
	Beards	35.0	...	...	...	...	...

plants contain 20 or more p.p.m. Mo, whereas with no cattle difficulty the Mo content of the plants was less than 10 p.p.m. Similarly the soils of affected areas contain the greatest amount of Mo, both total and water-soluble.

Results obtained by grazing cattle on adjacent plots planted to a single species, where the soil contained high soluble and total Mo, confirmed the conclusion that molybdenum is the cause of the disease. Only on the plots where the plant

TABLE 7

*Molybdenum content of Lotus corniculatus var. vulgaris as affected by application of ammonium molybdate to Aiken clay loam with a Mo content of 0.3 p.p.m.*

Mo ADDED TO SOIL	1ST CUTTING GROWN FROM NOVEMBER 27 TO MARCH 10		2ND CUTTING GROWN FROM MARCH 10 TO APRIL 13	
	Dry Matter per pot	Mo content	Dry matter per pot	Mo content
p.p.m.	gm.	p.p.m.	gm.	p.p.m.
0	1.68	2.1	0.99	3.3
10	1.54	149.5	0.89	301.5
50	1.89	342.5	1.03	516.7

TABLE 8

*Molybdenum content of dung from affected and recovered animals*

ANIMAL NUMBER	CONDITION OF ANIMAL	Mo IN DRY DUNG	ASH	Mo IN ASH
		p.p.m.	per cent	p.p.m.
1	Scouring June 25, 1946	63.8	26.5	248
1	Scouring stopped July 15, 1946	33.4	14.5	230
2	Scouring June 25, 1946	100.0	24.3	413
2	Scouring stopped July 17, 1946	29.7	16.7	178
3	Scouring June 25, 1946	60.0	26.6	225
3	Scouring stopped July 15, 1946	23.0	15.8	146
4	Scouring June 25, 1946	29.0	26.0	112
4	Scouring stopped July 17, 1946	16.3	37.0	44

species grown contained abnormally high Mo did the cattle show abnormal symptoms. The results of these plot experiments indicated that, by eliminating from the pasture plant species which absorb Mo to the greatest extent, it will be possible to establish wholesome pastures in these affected areas.

There seems to be evidence that for a given Mo content of the plant, the greater its succulence, the greater will be the injury to cattle. This seems to account for the fact that with Ladino clover as the chief plant in the pasture, and of which succulent leaves comprise a high percentage of that eaten by cattle, severe scouring has resulted where the plants contained as little as 15 p.p.m. Mo. Furthermore, young plants were found to be more injurious than mature plants, although the latter are higher in total Mo. The succulence of the plant appears



to be of particular importance when Mo content is from 10 to 20 p.p.m. In this range the effect of succulence on young calves appears to be particularly pronounced, perhaps because the calves graze largely on the leaves. Such calves should be given liberal amounts of dry feed as a supplement to the pasture.

It has been found that, by supplementing the pasture with liberal amounts of dry roughage, approximately normal condition of cattle can be maintained, even when the pasture plants contain as much as 100 p.p.m. For example, cattle severely affected by grazing on Ladino clover which contained 100 p.p.m. Mo, soon showed marked improvement when given dry grass hay containing 2 p.p.m. Mo. The Mo content of the dung of these animals before and after the supplemental feeding is shown in table 8. It is seen that not only did the Mo content of the dung decrease following the feeding of dry hay, but also the organic content of the dung increased, as indicated by the decrease in the ash content.

#### DISCUSSION

The foregoing results strongly indicate that the peculiar abnormality shown by cattle when grazing in certain areas of the San Joaquin Valley of California is caused by excessive Mo in certain species of plants. These were found to be chiefly legumes, which absorb considerably more Mo than nonlegumes.

It is interesting to note that although the high amounts of Mo which some of these plants contained were toxic to cattle, there was no indication of toxicity to the plant itself. Those with the highest Mo content were as healthy in appearance and as vigorous as those with the lowest Mo content. No doubt this may largely account for the fact that previously little or no thought was given to the possibility that something in the plants themselves might be involved in the cattle difficulty.

As judged by the Mo content of the dung, it appears that much of the Mo of the feed is thrown off by cattle by way of the alimentary tract. This can hardly mean, however, that none of the Mo is absorbed by the animal tissues. The general physiological condition of the affected cattle seems to preclude such a possibility.

It is surprising to find that the legumes and, in some instances, certain non-legumes absorb relatively much Mo from soil of extremely low total Mo content. This is believed to be due to the fact that the soil conditions favor relatively high solubility of the Mo present. The fact that these soils are alkaline is undoubtedly a factor in the solubility of Mo. Lewis (9) found that whether pasture plants grown on soils in England which contained approximately equal amounts of total Mo were toxic or nontoxic to cattle depended on the pH of the soil. If the pH was greater than 7, cattle scoured badly; if less than 7, this was not the case. It is probable, however, that the general kind of Mo compounds in the soil is also a factor. At present a study is being carried out to determine the nature of the molybdenum in the soil and the conditions which affect the absorption of the Mo by the plants.

The results of the investigation reported herein confirm the findings of Ferguson, Lewis, and Watson (7) in England. The only important difference in

the results of the two investigations is that the California soils contain very much less total Mo than the English soils.

#### SUMMARY

It was found that legumes growing on soil in the San Joaquin Valley of California, where cattle are abnormally affected, apparently always contain abnormally high amounts of Mo. Where symptoms of the disease are most pronounced, certain nonlegumes also contain toxic amounts of Mo.

The Mo content of legumes and nonlegumes alike appears to increase with the age of the plant.

The Mo content of the soils where the cattle disease is found is only slightly higher than is normally found in soils, but its solubility is relatively high. The alkalinity of these soils is partly responsible for the high solubility of the Mo.

Growing plants, particularly legumes, are able to absorb amounts of Mo harmful to cattle from soils that contain as little as 1.5–5.0 p.p.m. total Mo.

The greatest concentration of Mo was found, in most cases, in the blades of the leaves and in the actively growing plant parts.

Feeding dry roughage tended to reduce the excessive scouring to which cattle are subject when grazing on succulent leguminous pastures in the areas in question.

Excessive Mo in green plants seems, beyond reasonable doubt, to be decidedly toxic to young calves. It is unquestionably toxic to older animals. This was found to be the case even where there was no evidence of injury to the plants themselves.

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## TOXIC ASPECT OF MOLYBDENUM IN VEGETATION

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Ter Meulen (5), Bertrand (2), and others have shown that molybdenum is generally present in vegetation. The teart disease of cattle in Somerset, England, has been ascribed by Ferguson *et al.* (4) to the presence of 20 or more p.p.m. molybdenum in green pasturage. Britton and Goss (3) reported a case of chronic molybdenum poisoning in cattle in Kern County, California. This was caused by alfalfa pasturage containing 10.3 p.p.m. molybdenum.

Ferguson *et al.* (4) have brought out the important point that molybdenum is taken up by vegetation under alkaline soil conditions and that very little is taken up under acid soil conditions. In this respect, molybdenum behaves similarly to selenium and quite the opposite from manganese, boron, zinc, and copper. Soil that is overlimed may produce toxic green pasturage even in humid regions, provided the soil contains enough molybdenum.

Thus far, molybdenum toxicity has been noted only in cattle and then only with green pasturage. Dried hay containing similar quantities of molybdenum seems to be wholesome.

Recent work in this Bureau has shown that many soils produce vegetation high enough in molybdenum to be toxic to cattle. It would seem that the 20 p.p.m. lower limit set by the British (4) is too high, and it is believed that borderline cases may occur with very much lower quantities.

Table 1 shows the molybdenum oxide content (as  $\text{MoO}_3$ ) of a number of vegetation samples at our disposal. It will be seen that all the samples from a high selenium area in South America are also very high in molybdenum. Peas and grains from this area are highly toxic to cattle and humans. This toxicity has been ascribed to selenium (1). The selenium content of grains in this region exceeds 100 p.p.m. The question is raised as to what part molybdenum plays in the observed toxicity of grains from this area.

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TABLE 1  
Molybdenum content of various samples of vegetation  
Dry-weight basis

VEGETATION	MoO <sub>3</sub> CONTENT
	<i>p.p.m.</i>
Peas, seed, high selenium area, Colombia, S. A.....	137.0
Pinon pine, needles and twigs, Morrison sandstone, Colorado.....	15.7
Barley, seed, high selenium area, Colombia, S. A.....	13.8
Corn, seed, high selenium area, Colombia, S. A.....	12.6
Peanuts, kernels, Falls Church, Virginia.....	12.3
Wheat, high selenium area, Colombia, S. A.....	11.0
Alfalfa hay, Yuma, Arizona.....	9.4
Juniper, needles and twigs, Morrison sandstone, Colorado.....	9.3
Quack grass hay, Circle, Alaska.....	9.2
Peas, seed, wrinkled, Falls Church, Virginia.....	7.4
Bermuda grass, Yuma, Arizona.....	5.9
Pea vines, in bloom and early seeding, Falls Church, Virginia.....	5.7
Pea-oat silage, Fairbanks, Alaska.....	5.6
Bluetop, Fairbanks, Alaska.....	4.8
Oat plant, Fairbanks, Alaska.....	4.8
<i>Atriplex canescens</i> , Paradox Valley, Colorado.....	4.1
Russian thistle, Lyman County, South Dakota.....	3.8
Alfalfa, Beltsville, Maryland.....	3.7
<i>Thlaspi arvense</i> , Fargo, North Dakota.....	3.7
Alfalfa hay, Fredericksburg, Virginia.....	3.0
Collards, Norfolk, Virginia.....	2.8
Juniper, needles and twigs, Morrison sandstone, Colorado.....	2.6
Oleander leaves, Trona, California.....	2.6
Spinach, Falls Church, Virginia.....	2.5
Mixed grass, Fredericksburg, Virginia.....	2.0
Athel leaves, Trona, California.....	1.6
Cabbage, entire head, Falls Church, Virginia.....	1.6
Alfalfa, hay, Howard County, Maryland.....	1.4
Alfalfa, hay, Howard County, Maryland.....	1.4
Cabbage, Clemson, South Carolina.....	1.3
Carrots, roots, Falls Church, Virginia.....	1.3
Alfalfa hay, Brown Summit, North Carolina.....	1.1
Juniper, needles and twigs, South Dakota; Sandstone, Colorado.....	1.1
Pinon pine, needles and twigs, South Dakota; Sandstone, Colorado.....	1.0
Alfalfa hay, Howard County, Maryland.....	0.9
Alfalfa, Elliston, Virginia.....	0.9
Cabbage, entire head, Auburn, Alabama.....	0.9
Flowering Tamarisk, Trona, California.....	0.9
Kale, Norfolk, Virginia.....	0.9
Hickory leaves, Eaton, Indiana.....	0.9
Alfalfa hay, Howard County, Maryland.....	0.8
Spinach, Norfolk, Virginia.....	0.6
English walnut leaves, Riverside, California.....	0.6
Asparagus, in bloom and early seed, Falls Church, Virginia.....	0.3
Locust leaves, Falls Church, Virginia.....	0.3
Irish potato, tubers, Falls Church, Virginia.....	Trace
<i>Lespedeza sericea</i> , Falls Church, Virginia.....	Trace
Corn, seed, Ash Grove, Virginia.....	None detected
Scrub oak leaves, Dublin, Maryland.....	None detected
Hickory leaves, Takoma Park, Maryland.....	None detected



# RAPID CONDUCTOMETRIC METHOD FOR ESTIMATING GYPSUM IN SOILS<sup>1</sup>

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The gypsum content of soil is commonly estimated by determining calcium and sulfate in a water extract of the soil made at a sufficiently high moisture content to dissolve all the gypsum. Though this procedure gives satisfactory results, it involves quantitative determinations of two separate ions and hence is time-consuming. There is considerable need for a simpler and more rapid method for determining gypsum in soils. The purpose of this paper is to present a method in which gypsum is determined conductometrically following its separation from the other salts in a soil-water extract. The separation of gypsum is based upon its low solubility in an aqueous solution of acetone.

## METHOD

### *Apparatus*

1. A Wheatstone bridge for measuring alternating current resistance and a conductivity cell. Bridges are commercially available which utilize a 2-ml. capacity conductivity cell and give the conductivity reading directly in millimhos per centimeter. These bridges also are equipped with a temperature compensation dial so that no additional correction for temperature is required.

2. A centrifuge and 50-ml. capacity conical centrifuge tubes.

### *Reagent*

Acetone, reagent grade, boiling range 55.5 to 57.5° C.

### *Procedure*

Weight 10 to 20 gm. of air-dried soil<sup>3</sup> which has been passed through a 2-mm. round-hole sieve into an 8-ounce bottle and add a measured volume of distilled water sufficient to dissolve the gypsum present<sup>4</sup>. Stopper the bottle and shake

<sup>1</sup> Contribution from the U. S. Regional Salinity Laboratory, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, Riverside, California, in cooperation with the eleven Western States and the Territory of Hawaii.

<sup>2</sup> Soil scientist and scientific aid, respectively.

<sup>3</sup> The soil should not have been oven-dried, as heating at 105° C. converts  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ . The latter hydrate has a higher solubility in water for an indefinite period following its solution (4).

<sup>4</sup> The water at a 1:5 soil-water ratio will dissolve approximately 15 m.e. of gypsum per 100 gm. of soil. If, by the use of a 1:5 soil-water extract, it is found that the gypsum content of the soil approaches 15 m.e. per 100 gm., the determination should be repeated, using a more dilute extract.

by hand six times at 15-minute intervals, or agitate for 30 minutes in a mechanical shaker. Filter the extract through paper of medium porosity. Transfer a 20-ml. aliquot of the filtered extract containing 0.1 to 0.6 m.e. of  $\text{CaSO}_4$  into a 50-ml. conical centrifuge tube. Add 20 ml. of the acetone and mix the contents of the tube. Let stand until the precipitate flocculates. This usually requires 5 to 10 minutes. Centrifuge at a force of about 1,000 times gravity for 3 minutes, decant the supernatant liquid, invert the tube and drain on filter paper for 5 minutes. Disperse the precipitate and rinse the wall of the tube with a stream of 10 ml. of the acetone blown from a pipette. Again centrifuge at a force of approximately 1,000 times gravity for 3 minutes, decant the supernatant liquid, invert the tube and drain on filter paper for 5 minutes. Add exactly 40 ml. of distilled water to the tube, stopper, and shake until the precipitate is completely dissolved. Measure the electrical conductivity of the solution by means of a conductivity cell and Wheatstone bridge. Correct the conductivity reading to 25° C., using a correction factor of 2 per cent per degree C.<sup>5</sup> Determine the concentration of  $\text{CaSO}_4$  in the solution by reference to a graph showing the relationship between the concentration and the electrical conductivity of  $\text{CaSO}_4$  solutions. This graph may be constructed by means of the following data from the International Critical Tables (1, pp. 231, 236):

<i>CaSO<sub>4</sub> concentration, m.e./liter</i>	<i>Electrical conductivity at 25°C, millimhos/cm.</i>
1	0.121
2	0.226
5	0.500
10	0.900
20	1.584
30.5	2.205

#### Calculations

m.e. of  $\text{CaSO}_4$  in aliquot = [(m.e./liter of  $\text{CaSO}_4$  from conductivity reading)  $\times$  (ml. of water used to dissolve precipitate)]  $\div$  1,000.

m.e. of  $\text{CaSO}_4$ /100 gm. of soil = [100  $\times$  (m.e. of  $\text{CaSO}_4$  in aliquot)]  $\div$  [(soil to water ratio  $\times$  (ml. of soil-water extract used))].

#### EXPERIMENTAL

##### *Influence of various ions on the conductometric method*

Eight standard salt solutions were used to study the effects of various ions upon the proposed method. The ionic compositions of the standard salt solutions, the concentrations of  $\text{CaSO}_4$  present, and the concentrations of  $\text{CaSO}_4$  found upon analysis by the conductometric method are given in table 1. As shown by the data for solutions 1 to 3, of the ions present in concentrations of 50 m.e. per liter, only potassium interfered with the determination. At this

<sup>5</sup> The formula  $EC_{25} = EC_t[1 + 0.02(25 - t)]$ , where  $EC_{25}$  is the electrical conductivity at 25°C. and  $EC_t$  is the electrical conductivity at the observed temperature,  $t$ , may be used in making this correction.

concentration,  $K_2SO_4$  caused high results. The minimum of potassium effecting interference was investigated by means of solutions 4 to 8, in which the potas-

TABLE 1

*Influence of various ions on the conductometric determination of  $CaSO_4$  in standard salt solution*

SOLUTION NO.	COMPOSITION OF STANDARD SALT SOLUTIONS							CaSO <sub>4</sub> PRESENT IN STANDARD SOLUTION	CaSO <sub>4</sub> FOUND BY ANALYSIS
	Ca	Mg	Na	K	SO <sub>4</sub>	Cl	NO <sub>3</sub>		
	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.
1	15.1	50	50	...	65.1	50	...	15.1	15.0
2	15.1	...	...	50	65.1	...	...	15.1	40.0
3	65.1	...	...	...	15.1	...	50	15.1	15.0
4	14.7	...	...	5	19.7	...	...	14.7	14.6
5	14.7	...	...	10	24.7	...	...	14.7	14.8
6	14.7	...	...	15	29.7	...	...	14.7	17.4
7	14.7	...	...	20	34.7	...	...	14.7	22.6
8	14.7	...	...	25	39.7	...	...	14.7	27.0

TABLE 2

*Ionic composition of water extracts of 10 soil samples*

SOIL			SOIL: WATER RATIO	SOLUBLE IONS IN SOIL-WATER EXTRACT							
No.	Type	Depth		Ca	Mg	Na	K	CO <sub>3</sub> +HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>
		inches		m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.
711	Umapine loam	0-6	1:5	1.8	0.1	8.4	<1	4.8	4.0	2.0	tr.
749	Sagemoor fine sandy loam	0-6	1:5	6.4	3.0	39.3	<1	1.9	28.2	10.2	5.8
2282	Holtville silty clay loam	0-12	1:10	6.7	1.1	37.6	<1	1.2	24.0	17.8	tr.
574	Billings clay loam	0-9	1:10	7.1	3.7	8.0	<1	0.7	13.3	3.8	tr.
698	Oasis silty clay loam	12-24	1:5	15.4	6.1	19.9	<1	1.1	30.4	8.0	tr.
589	Billings clay loam	12-18	1:5	22.0	2.9	18.8	<1	0.5	35.6	4.5	tr.
773	Esquatzel loam	6-12	1:10	12.4	4.5	22.7	<1	0.9	28.4	4.3	2.7
772	Esquatzel loam	0-6	1:10	16.7	1.9	31.1	<1	1.2	40.4	6.8	tr.
513	Indio clay	0-10	1:20	14.8	0.5	11.4	<1	0.5	19.7	5.3	tr.
85	Reagan clay loam	2-8	1:25	12.4	1.7	0.9	<1	0.4	13.8	0.5	tr.

sium concentration varied from 5 to 25 m.e. per liter. The results show that potassium does not interfere until its concentration in the solution exceeds 10 m.e. per liter. Since the potassium concentration of soil-water extracts rarely

exceeds this value, the interference does not constitute a serious objection to the method.

TABLE 3

*Comparison of standard and conductometric methods for determination of  $\text{CaSO}_4$  in soil-water extracts*

SOIL NO.	CaSO <sub>4</sub> IN SOIL-WATER EXTRACT						GYPSUM CONTENT OF SOILS	
	SO <sub>4</sub> in excess			Ca in excess			Standard method	Conductometric method
	Standard method	Conductometric method	Difference	Standard method	Conductometric method	Difference		
	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./100 gm.	m.e./100 gm.
711	1.8	1.6	-0.2	4.0	4.2	0.2	0.9	0.8
749	6.4	6.4	0.0	28.2	28.0	-0.2	3.2	3.2
2282	6.7	7.1	0.4	24.0	24.0	0.0	6.7	7.1
574	7.1	7.0	-0.1	13.3	13.3	0.0	7.1	7.0
698	15.4	15.4	0.0	30.4	30.2	-0.2	7.7	7.7
539	22.0	22.4	0.4	35.6	36.0	0.4	11.0	11.2
773	12.4	12.8	0.4	28.4	29.0	0.6	12.4	12.8
772	16.7	17.0	0.3	40.4	40.0	-0.4	16.7	17.0
513	14.8	14.9	0.1	19.7	20.4	0.7	29.6	29.8
85	12.4	11.8	-0.6	13.8	13.8	0.0	31.2	29.5
Average.....	11.57	11.64		23.78	23.89			
Standard deviation of differences by "Student's" method.....	0.307			0.342				

TABLE 4

*Effect of temperature on the conductometric determination of  $\text{CaSO}_4$  in soil-water extracts*

SOIL NO.	CaSO <sub>4</sub> IN SOIL WATER EXTRACT		
	16°C	24°C	38°C
	m.e./l.	m.e./l.	m.e./l.
513	15.0	14.9	14.8
574	7.1	7.0	6.9
772	17.1	17.0	16.8

#### *Comparison of standard and conductometric methods*

The accuracy of the conductometric method, when applied to soil-water extracts, was compared with that of the usual method involving separate determinations of calcium and sulfate. Samples of ten soils were extracted with sufficient water to dissolve the gypsum present, and determinations were made on the extracts by the two methods. The soils used, the soil-water ratio employed, and the ionic composition of the extracts are given in table 2. With the ex-

ception of sulfate, which was determined gravimetrically as  $\text{BaSO}_4$ , the methods described by Reitemeier (2) were used for the determination of the various ions. It will be noted that sulfate exceeds calcium in all the extracts. To permit evaluation of the conductometric method when calcium exceeds sulfate, solid  $\text{CaCl}_2$  (1 m.e. per 20 ml. of extract) was added to portions of each extract. The  $\text{CaSO}_4$  contents of the two sets of extracts as determined by the two methods are given in table 3. The results of the comparison show that the conductometric method gives reasonably accurate results and that none of the common soluble ions found in soil interferes with the determination. The method appears to be somewhat more accurate when calcium exceeds sulfate.

#### *Effect of temperature on the conductometric method*

The determinations reported in table 3 were made at a temperature of approximately 24° C. To obtain information on the effect of higher and lower temperatures on the accuracy of the method, determinations were made on the extracts from three soils at 16° and 38° C. As shown in table 4, the determination is slightly affected by temperature. The best agreement between values obtained by the standard and conductometric methods occurred at 16° C. in soil 574, and at 38° C. in soils 513 and 772. It is apparent, therefore, that errors due to temperature variations are within the limits of the accuracy of the method.

#### DISCUSSION

The precise determination of gypsum in soils is made difficult, if not impossible, by inherent errors involved in extraction of the mineral by water. Studies conducted by Reitemeier (3) show that, upon addition of water to gypsiferous soils, at least three factors besides solution of gypsum may influence the amounts of calcium and sulfate extracted. They are: (a) the solution of calcium from sources other than gypsum, for example,  $\text{CaCO}_3$ , (b) exchange reactions in which soluble calcium replaces other cations such as sodium and magnesium, and (c) the solution of sulfate from sources other than gypsum. In view of these errors involved in the extraction of gypsum from soils by water, the proposed method is considered to be satisfactory for most soil analysis.

Addition of an equal volume of acetone to an aliquot of a soil-water extract constitutes a simple qualitative test for the presence of gypsum in soils. This test may be made semiquantitative by comparing the turbidity of the unknown suspension with that produced by adding acetone to solutions containing known amounts of gypsum. Such tests may be of value to soil surveyors and others concerned with the examination of soils in the field.

#### SUMMARY

A rapid method for estimating gypsum in soils is presented in which the gypsum is determined conductometrically following its separation from the other salts in a soil-water extract by the addition of acetone. The results of determinations made on ten soil extracts by the proposed method agree satisfactorily with those obtained by the usual method involving the separate determination of calcium and sulfate.



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# DETERMINATION OF THE CRITICAL STREAM FOR VARIOUS SLOPES<sup>1</sup>

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Soil erosion is a serious problem in many areas and has received considerable attention from soil scientists in public and private agencies. A large part of the work done has been of an engineering nature where field studies have been made and remedies applied as experience has dictated. The essential weakness in these studies is that, as a rule, no attempt is made to use the analytical attack and for that reason many of the experimental data have local significance only. Some attempts have been made, however, to use mathematics in an effort to obtain generalizations. Lutz and Hargrove<sup>3</sup> have suggested an explicit relationship between the erosion and various factors such as particle size, discharge, depth, and slope, but inasmuch as they consider soil separates, they do not obtain significant soil parameters characteristic of field soils.

Horton<sup>4</sup> has presented a "rational" formula,

$$f(S) = \frac{\sin \alpha}{\tan^{0.3} \alpha},$$

where  $f(S)$  is proportional to the eroding force,  $S$  is the slope, and  $\alpha$  is the slope angle. He seems, however, to have overlooked the fact that only a fractional part of the energy dissipated by the stream is used in disintegrating the soil and that this fraction may be greater when the velocity is high, as is the case with water running on steep slopes. The size of the irrigation stream decreases with distance down the slope, whereas the stream fed by falling rain may increase rapidly down the slope, the rate of erosion increasing as the slope along the stream decreases. An equation,

$$q_c = b/s^\gamma,$$

proposed by Gardner and Lauritzen<sup>5</sup> indicates that the critical stream, that is, the size of stream above which the soil continues to wear down indefinitely, approaches zero as  $s$  approaches infinity. Experimental data here presented were obtained on very small slopes and therefore should be consistent with either of

<sup>1</sup> Contribution from the physics department, Utah Agricultural Experiment Station.

<sup>2</sup> Research fellow.

<sup>3</sup> Lutz, J. F., and Hargrove, B. D. Soil movement as affected by slope, discharge, depth and velocity of water. N. C. Agr. Exp. Sta. and Soil Conserv. Serv. U. S. Dept. Agr. Tech. Bul. 78. 1944.

<sup>4</sup> Horton, R. E. Erosional development of streams and their drainage basins; hydro-physical approach to quantitative morphology. *Bul. Geol. Soc. Amer.* 56: 275-370. 1945.

<sup>5</sup> Gardner, W. and Lauritzen, C. W. Erosion as a function of the size of the irrigating stream and the slope of the eroding surface. *Soil Sci.* 62: 233-242. 1946.

the two theories. It does not seem likely, however, that the erosion rate should reach a maximum at 45 degrees (the slope being equal to 1), as Horton's theory implies.

Considerably more work has been done by hydraulic engineers on the mechanics of eroding forces, such as the work of Van Driest<sup>6</sup> on turbulence diffusion. Nielsen<sup>7</sup> has reported the results of a field study in which the influence of slope on erosion in small irrigation furrows was investigated.

The analytical attack on the problem of eroding irrigation streams by Gardner and Lauritzen is founded on the equation of continuity and should therefore be fundamentally sound. Experimental data are required to relate the silt content of the water for the ideal case to the distance along the stream and the time, and if a successful empirical equation is obtained the procedure of these workers leads immediately to a first order partial differential equation giving the rate at which the soil wears down as a function of the distance down the slope  $x$  and the time  $t$ . It is evident that this equation will involve certain soil parameters, the size of the stream, and the slope of the eroding surface.

It should be apparent that there must exist an ideal equation expressing the critical size of stream ( $q_c$ ) as a function of the slope and of various soil parameters. It should be regarded as fortunate if the simple equation of Gardner and Lauritzen should prove to be a good first approximation. This combined with appropriate empirical equations giving the velocity of the stream as a function of its size, the slope, and appropriate soil parameters, should constitute a very satisfactory theoretical approach to the problem.

Gardner and Lauritzen have given tentative values, for the constants in their equation, of 1.3 for  $\gamma$  and  $4.22 \times 10^{-5}$  cubic feet per second per unit width of irrigation strip for  $b$  for Millville silt loam.<sup>8</sup> From a practical point of view their formula provides a means for estimating for a particular slope the point above which the irrigation stream must not be raised if continuous erosion is to be prevented, and expresses in mathematical form a fact observed by farmers and soil experimenters that a stream, if kept small enough, will carry away little soil.

#### EXPERIMENTAL EQUIPMENT

The flumes used previously in obtaining the tentative values for  $\gamma$  and  $b$  given above were constant slope flumes and the experimental procedure was not sufficiently refined to give wholly reliable results. Equipment of a somewhat different type, which allows more precise measurement of the size of critical stream  $q_c$  and the slope  $s$ , has been developed in this project.

<sup>6</sup> Van Driest, E. R. Experimental investigation of turbulence diffusion—a factor in transportation of sediment in open channel flow. *Jour. App. Mechanics*. 12: A91-A100. 1945.

<sup>7</sup> Nielsen, H. E. The influence of slope on erosion in small irrigation furrows. 1941. [Unpublished thesis. Copy on file School of Engin., Utah State Agricultural Col., Logan.]

<sup>8</sup> Called *Greenville silt loam* by Gardner and Lauritzen and other authors in early publications but more correctly classed as Millville silt loam.

The flume used (figs. 1, 3, and 4) is 4 feet long and 20 inches wide with a slope increasing in increments of 0.1 per cent for each 1.5 inches down the flume. A means is provided for tilting the flume to obtain more gradual or greater slopes. A baffle the same height as the soil depth is placed at the outlet end of the flume to minimize end-effect troubles.<sup>9</sup> Precise guide rails are placed on the edges of the flume and a precisely straight, parallel edged scraper blade is made to ride on them and level the soil. By use of a level on its top edge, the scraper blade can be adjusted so that its bottom edge is horizontal at all times.

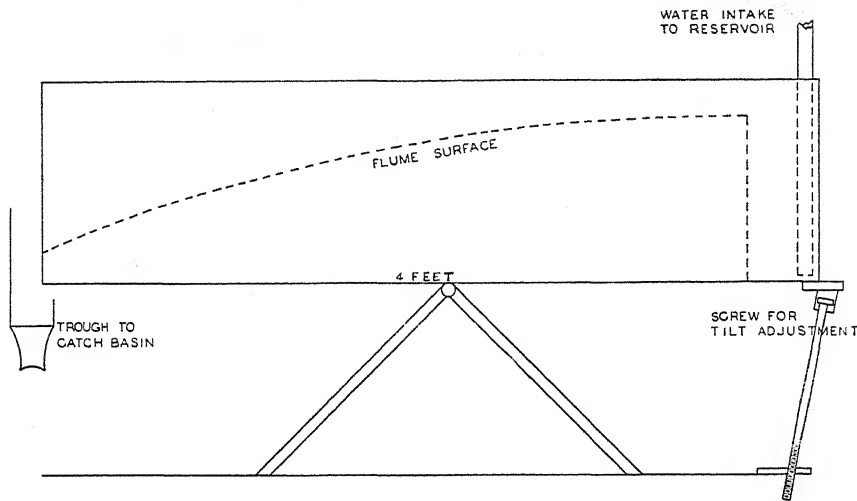


FIG. 1. DIAGRAM OF FLUME, SHOWING SLOPING SURFACE

Vertical dimension is exaggerated to show slope, which increases 0.1 per cent every  $1\frac{1}{2}$  inches down the flume.

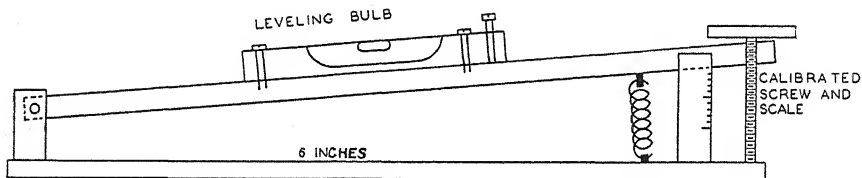


FIG. 2. DIAGRAM OF GONIOMETER FOR MEASURING FLUME AND SOIL SLOPES

Two different instruments were used for measuring slopes, a small goniometer (fig. 2) and an optical lever (figs. 3 and 5). The goniometer has a bearing plate 6 inches long and 1 inch wide and has a leveling bulb on a lever arm which can be adjusted with a fine screw. The precision is better than 0.05 per cent slope. In the later stages of the project an optical lever was devised to speed up reading of the slopes and to allow for a measurement of slopes in a narrower

<sup>9</sup> The term *end-effect* is used to describe erosion at an excessive rate on a steep frontal slope which, if allowed to start, creeps up the flume, obscuring the normal erosion pattern in the early stages of a run.

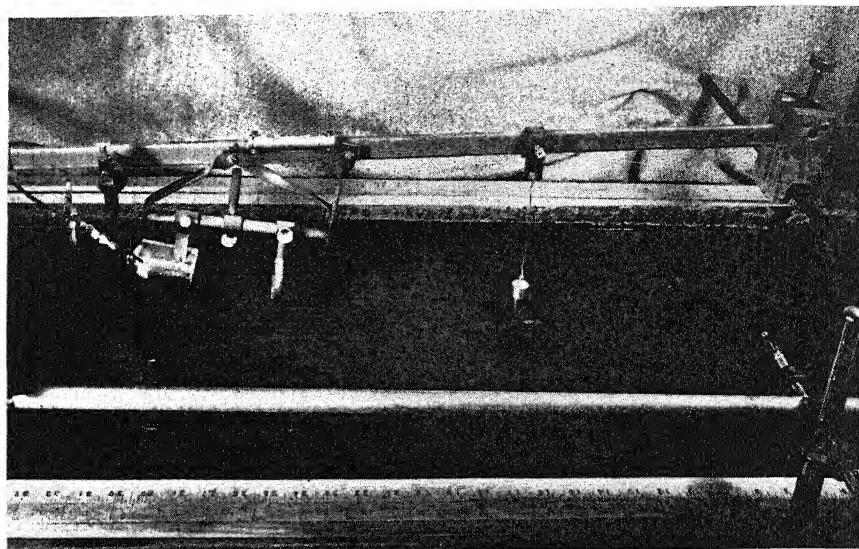


FIG. 3. EXPERIMENTAL FLUME SHOWING OPTICAL LEVER IN PLACE  
Photograph by H. Reuben Reynolds

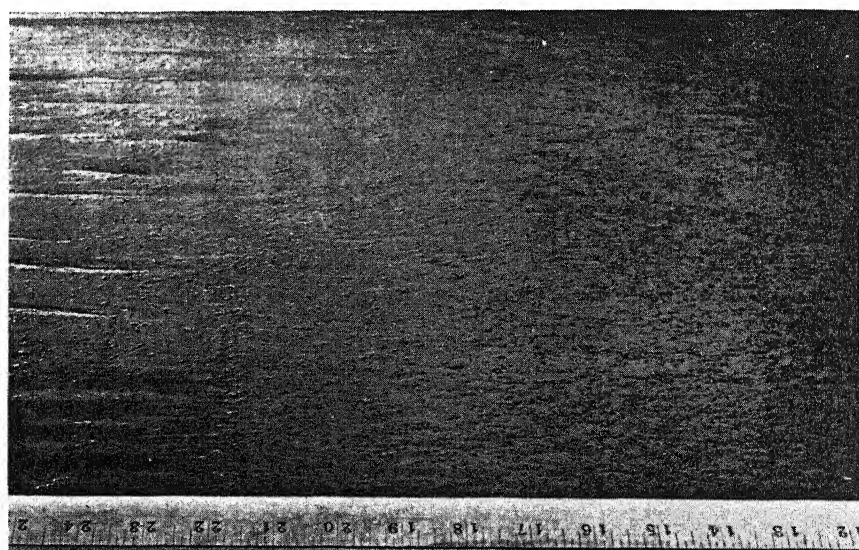


FIG. 4. SOIL SURFACE DURING TEST, SHOWING ZONE CHARACTER  
Photograph by H. Reuben Reynolds

region. The optical lever consists in part of an automobile head-lamp with a very fine cross hair mounted in front of it. The beam and the cross hair are projected through a 9-cm. focal length lens onto a very thin water film covering the surface of the soil at the point of measurement and then reflected to a meas-



uring scale 188 cm. away. The angle of incidence of the beam  $\phi$  is 12.5 degrees from the horizontal. The displacement of the reflected beam is a measure of the change in slope. A leveling bulb and two adjusting screws for leveling and for displacing the system vertically are used. A plumb bob hung from the support arm furnishes a reference point for adjusting the point of incidence of the beam on the soil surface. The entire optical lever is placed on a rectangular framework so as to permit motion laterally and up and down the flume to any desired point. The optics of the system are such that the angle of tilt of the

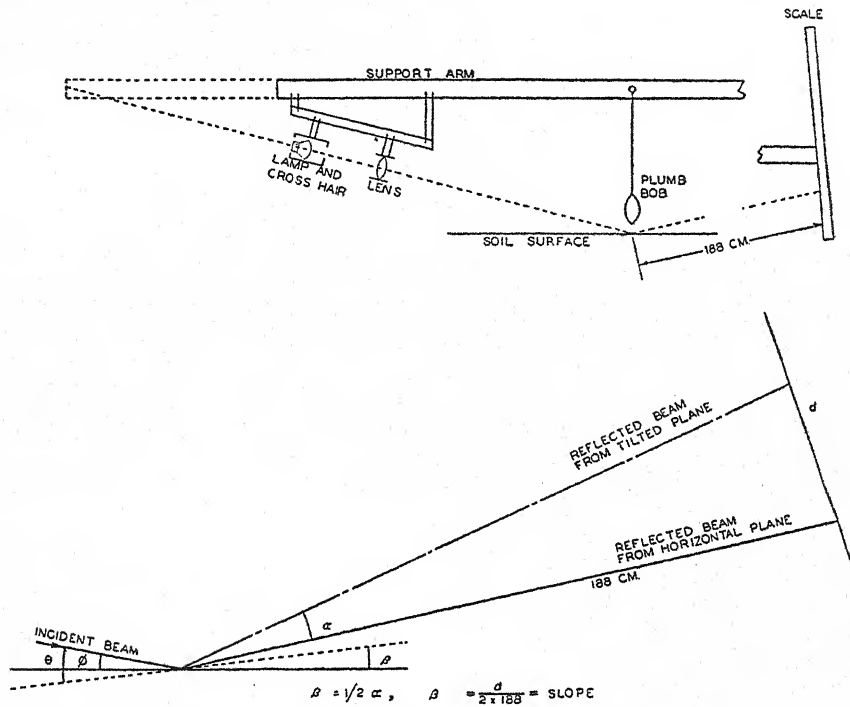


FIG. 5. PHYSICAL ARRANGEMENT AND OPTICS OF OPTICAL LEVER FOR MEASURING THE SLOPE OF THE SOIL

reflecting plane is multiplied by a factor of 2 in the reflected beam (fig. 5). An additional leverage is gained by placing the measuring scale at a distance of 188 cm., which permits a precision of 37.6 mm. per 1 cent change in slope. The zero adjustment is made by taking a reading on the stable water surface at the head of the flume. The over-all accuracy of the instrument is no less than  $\pm 0.01$  per cent slope.

The chief advantage of the optical lever over the goniometer for measuring slopes is that it permits making as many slope readings as are desired during the course of a run on a single sample of soil. The goniometer required a partly dry, firm surface which could be obtained only by allowing the soil to dry for

approximately 12 hours. Also only a single set of readings could be taken on a single soil sample when slopes were read with a goniometer.

#### EXPERIMENTAL PROCEDURE

The soil is prepared by air-drying and screening through what corresponds approximately to a number 10 sieve (the Millville soil requires grinding before screening). The soil in this condition is placed on the flume and spread evenly with the scraper blade to a uniform thickness of  $\frac{5}{32}$  of an inch. Before the test is begun, the soil is wetted by applying a small stream of water at the upper end and allowing it to creep down the flume largely under the influence of capillary attraction. Water at any desired constant rate is supplied from a fixed-head tank.

The initial procedure was to allow water to run down the flume at a constant  $q$  for what was thought to be a sufficient length of time for equilibrium to be reached (3 to 5 hours, depending on the soil and the size of stream). Shortly after the water is started down the flume the soil generally assumes a physical pattern characterizing the erosion at the various slopes in the flume. Four zones develop (fig. 4), usually discernible but sometimes much more distinct than at other times, depending on the particular soil and the size of stream.<sup>10</sup> These zones are briefly described as follows:

- Zone of gulying: in which erosion occurs at such a rate that gulying usually results.
- Zone of erosion: in which erosion proceeds at rapid rate but not sufficient to gully.
- Zone of transition: zone between the areas of definite erosion and of no erosion, characterized by a mottled surface, partly the color of the rapidly eroding soil and partly the color of the uneroded soil.
- Zone of no erosion: in which the soil is undisturbed.

After the stream is stopped, the soil is allowed to dry overnight so that the surface becomes firm enough to support the goniometer used to measure the critical slope (i.e., the point in the flume where the slope is just great enough to permit erosion and above which no erosion takes place—ideally the asymptote of a curve obtained by plotting the slope in the transition zone as a function of the time of run).

As inferred above, the slope in the transition zone changes with time. This is because the soil depth is finite and as erosion proceeds on the steeper portions of the flume a frontal surface is formed which gradually moves up the flume even though the slope of the undisturbed soil itself is below the critical value. As the frontal surface moves up the flume, the slope of the flume is becoming less and less and the slope of the frontal surface approaches the critical slope at a slower and slower rate. At time infinite, the slope of this frontal surface might be expected to be at the critical value, with the surface itself intersecting the uncovered flume and the undisturbed soil surface. This is illustrated by the curves of figures 6, 7, and inset 8.

<sup>10</sup> Trenton fine sandy loam, on which some tests have been run, does not show up the zone character as does Millville silt loam. By illuminating the surface from an oblique source of light, however, it is possible to find the zone of transition.

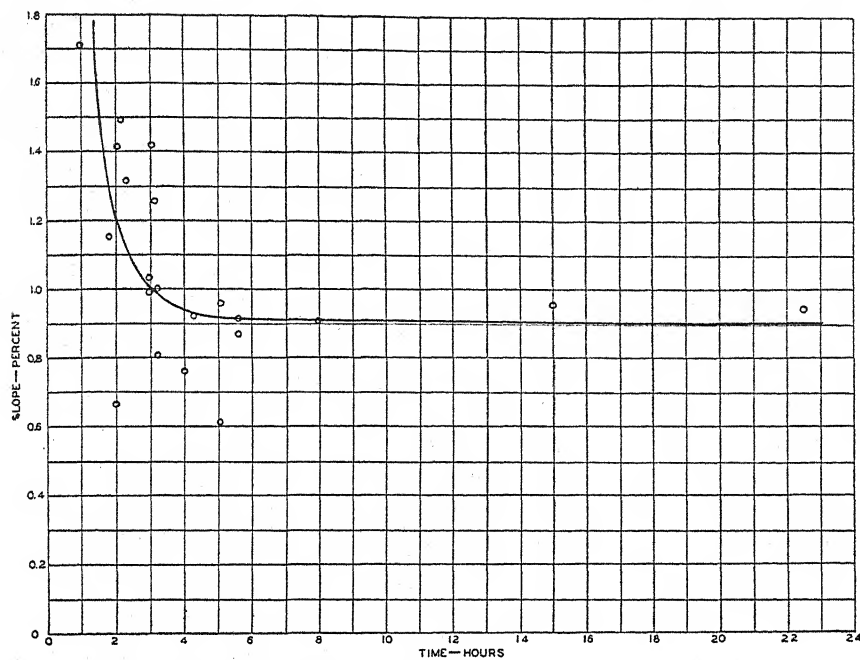


FIG. 6. CURVE SHOWING SLOPE AT TRANSITION ZONE FOR MILLVILLE SILT LOAM  
AS MEASURED WITH A GONIOMETER  
 $q = 0.002$  cubic feet per second

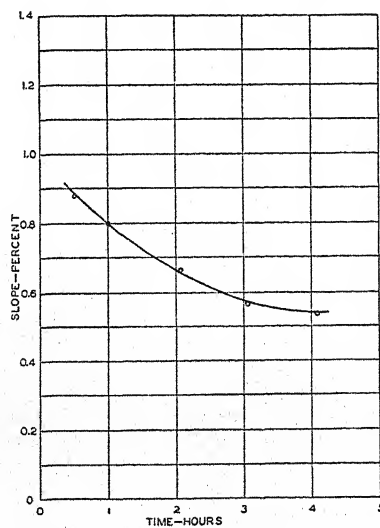


FIG. 7. CURVE SHOWING SLOPE AT TRANSITION ZONE FOR MILLVILLE SILT LOAM  
AS MEASURED WITH OPTICAL LEVER  
 $q = 0.00345$  cubic feet per second

As a check on the visual method of picking the transition zone, curves were made by plotting the slope as a function of the distance from the water intake with time as a parameter (fig. 8). These curves approximate the original soil slope up to the point where erosion has taken place and then take a decided jump to much greater values. The point on these curves at which maximum curvature occurs corresponds to the zone of transition selected visually. By plotting the slope at the point of maximum curvature against time, a curve (inset fig. 8)

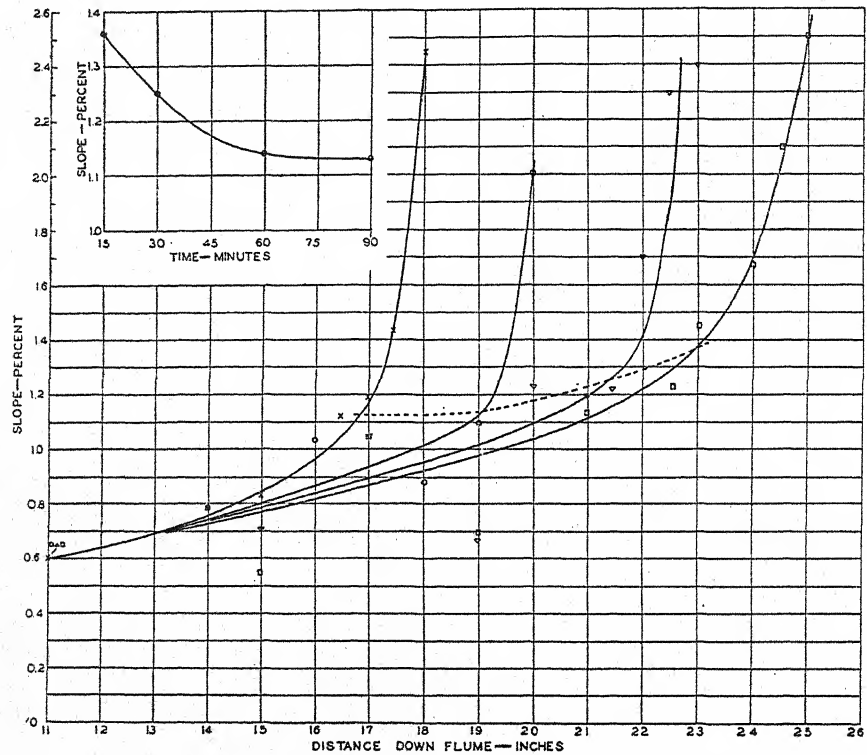


FIG. 8. CURVES SHOWING SLOPE AS A FUNCTION OF DISTANCE FROM WATER INTAKE WITH TIME OF RUN AS A PARAMETER

Inset shows a curve of slopes at maximum curvature as a function of time of run

of the same type as those of figures 6 and 7 is obtained. A curve of the slope in the transition zone plotted as a function of the distance from the water intake is obtained by connecting these points of maximum curvature on the four curves (broken line in figure 8). This curve, too, seems to be approaching an asymptote.

Not all the data presented here have been obtained by computing the value of the asymptote on curves such as those shown in figures 6 and 7. A time of run has been determined from inspection of a number of these curves so that the measured slope in the transition zone would be a reasonable approximation of the asymptote. It should also be noted that when the optical lever was used,

slopes at any point on the flume could be measured, without disturbing the experiment, during brief intervals when the stream was stopped.

TABLE 1  
*Mechanical analyses and pH values of three soils of different physical properties*

SOIL	PARTICLE SIZE DISTRIBUTION				DISPERSION	pH
	2-0.05 mm.	0.05-0.002 mm.	<0.002 mm.	<0.005 mm.		
	per cent	per cent	per cent	per cent	per cent	
Millville silt loam.....	30	56	14	23	20	7.9
Trenton fine-sandy loam.....	77	15	8	10	7	8.2
Oasis silt loam.....	6	64	30	58	95	8.5

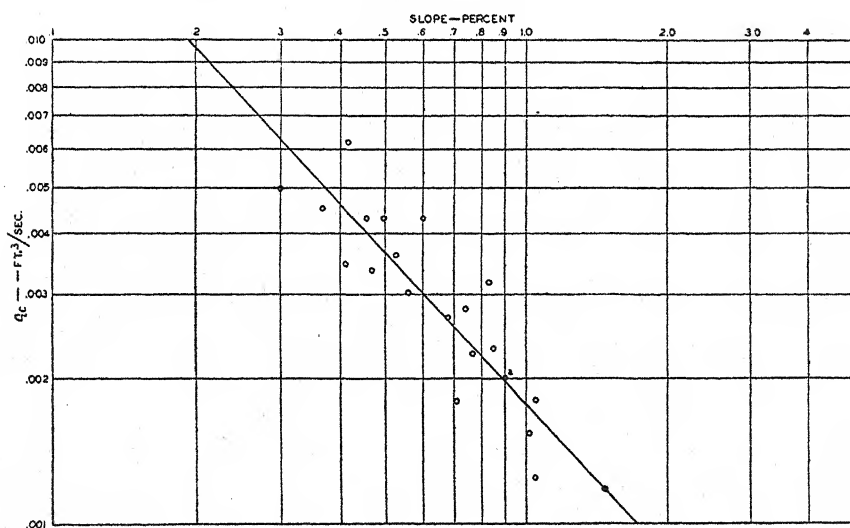


FIG. 9. CRITICAL STREAM-SLOPE CURVE FOR MILLVILLE SILT LOAM  
Slopes measured with goniometer

#### EXPERIMENTAL DATA AND REGRESSION CURVES

Data have been obtained for checking the equation

$$q_c = b/s^{\gamma}$$

on three different soils. The soils were selected for significant difference in their physical properties. The mechanical analyses and pH values for the three soils are shown in table 1.

The curve representing the data for Millville silt loam as taken with the surface goniometer, each point representing an individual run, is shown in figure 9. Point *a* on this curve is the asymptotic value obtained from the time curve of figure 6 and should therefore carry much more weight than the other points. A curve for the Millville soil made by use of the optical lever for meas-



urement of the slopes is shown in figure 10. The curves for Trenton fine sandy loam and Oasis silt loam are also shown in figure 10. A modified procedure involving use of parts of curves similar to those shown in figure 8 was used in obtaining the data in figure 10.

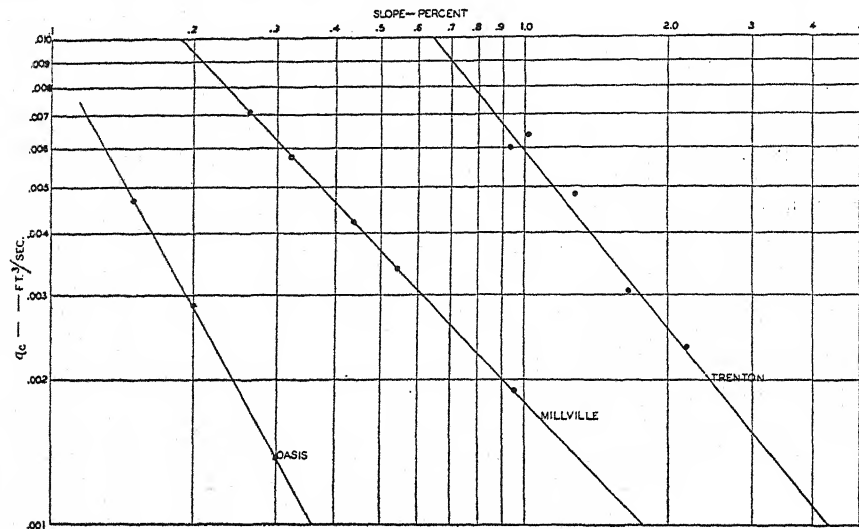


FIG. 10. CRITICAL STREAM-SLOPE CURVES FOR MILLVILLE SILT LOAM, TRENTON FINE SANDY LOAM, AND OASIS SILT LOAM  
Slopes measured with optical lever

TABLE 2

Values for  $\gamma$  and  $b$ , for three soils, from experimental data

SOIL	$\gamma$	$b^*$ FT. <sup>3</sup> /SEC. FT. WIDTH
Millville silt loam (Curve of figure 9).....	1.06	$1.45 \times 10^{-5}$
Millville silt loam (Curve of figure 10).....	1.03	$1.57 \times 10^{-5}$
Trenton fine sandy loam.....	1.22	$2.02 \times 10^{-5}$
Oasis silt loam.....	1.80	$3.97 \times 10^{-5}$

\* The constant  $b$  is the value of  $q_c$  at a slope of 1 (45°) computed mathematically or obtained graphically by extending the curve to the ordinate line where the slope is 1 and reading the corresponding  $q_c$ . This can be seen from the equation,

$$\log q_c = \log b - \gamma \log s.$$

The values for  $\gamma$  and  $b$  as obtained from the experimental data by the method of least squares are shown in table 2. It should be noted that these values are somewhat lower for the Millville soil than those reported tentatively by Gardner and Lauritzen (1.3 for  $\gamma$  and  $4.22 \times 10^{-5}$  cubic feet per second per unit width of flume). This is probably due to the different techniques used in selecting the critical slopes and the greater precision possible with the present equipment.

## CONCLUSIONS

The Gardner-Lauritzen equation,

$$q_c = b/s^\gamma,$$

seems to fit the experimental data. The data obtained here indicate, however, that the values for  $\gamma$  and  $b$  for Millville silt loam, given as tentative by Gardner and Lauritzen, require modification.

It is evident that soil parameters that will characterize a soil's erodibility do exist. The critical stream-slope equation together with these parameters may be used to determine the proper stream-size and soil-slope relationship for a particular soil in the ideal case. However, it would likely be very impractical for farmers to limit their irrigation streams to the low values given for no-erosion conditions, and in practice greater streams would be used. Nevertheless, such information on a soil should prove to be a useful guide to engineers and county agents in determining proper irrigation practices.

The equipment and experimental techniques developed in this project are of a simple nature and will permit fairly rapid measurement of the critical stream-slope relationship and determination of the numerical values of the parameters for various soils.



# A FABRIC ABSORPTION UNIT FOR CONTINUOUS MEASUREMENT OF SOIL MOISTURE IN THE FIELD<sup>1</sup>

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Previous publications (1, 2, 3, 5, 6, 8, 9, 10, 11) have shown that the plaster of paris electrical resistance method gives agronomists and plant physiologists a practical means of following field moisture changes in soils. The pore size distribution of plaster of paris is such that it measures soil moisture from field capacity down to the wilting point, through that range of soil moisture which is generally termed "available water."

Two characteristics, however, have limited the usefulness of this type of absorption unit. One disadvantage is that plaster of paris does not afford a wide range of sensitivity. Although plaster of paris absorption blocks are satisfactory tools for agronomists, who are primarily interested in available water, civil engineers and hydrologists seek a method that will measure the entire soil moisture range from saturation to air-dryness. A second limitation is encountered in continuously wet locations, where plaster of paris installations begin to disintegrate after functioning several months in saturated environments.<sup>3</sup> There is a great need for units that will function despite long periods of exposure to circulating ground water.

For these reasons, intensive research has been devoted to developing absorption units that will satisfy diverse requirements. A progress report published in 1941 (3) dealt with studies of fire-processed clays, cement and concrete mixtures, dental casting compounds, and other gypsum materials characterized by various pore-size distributions. Mentioned in the original publication (2, p. 5) was some early work indicating that certain plastics, then relatively new, might possibly provide satisfactory absorbent properties. In 1943 attention was focused on these plastics in a study that included various fabric and exploded and compressed fiber forms of rubber, resins, nylon, glass, and asbestos (5). During this period, samples of these materials were buried to determine their durability characteristics in field soil environments.

In 1946 Colman (7) suggested a soil-moisture meter with a fiberglas absorption unit.

<sup>1</sup> Contribution from the Soil Science Section of the Michigan Agricultural Experiment Station. Authorized for publication by the director as Journal Article No. 859.

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<sup>3</sup> Plaster of paris blocks have given excellent performance in better drained environments where they still function perfectly after seven seasons. These installations, extending to a depth of 6 feet in the Hillsdale, Conover, and Berrien series, have provided an uninterrupted daily index of soil moisture conditions, even though the last two profiles are imperfectly drained.

## ABSORPTION UNITS STUDIED

Figure 1 pictorially summarizes 25 different kinds of the more important electrode absorption units that have been investigated. Units 1 through 10

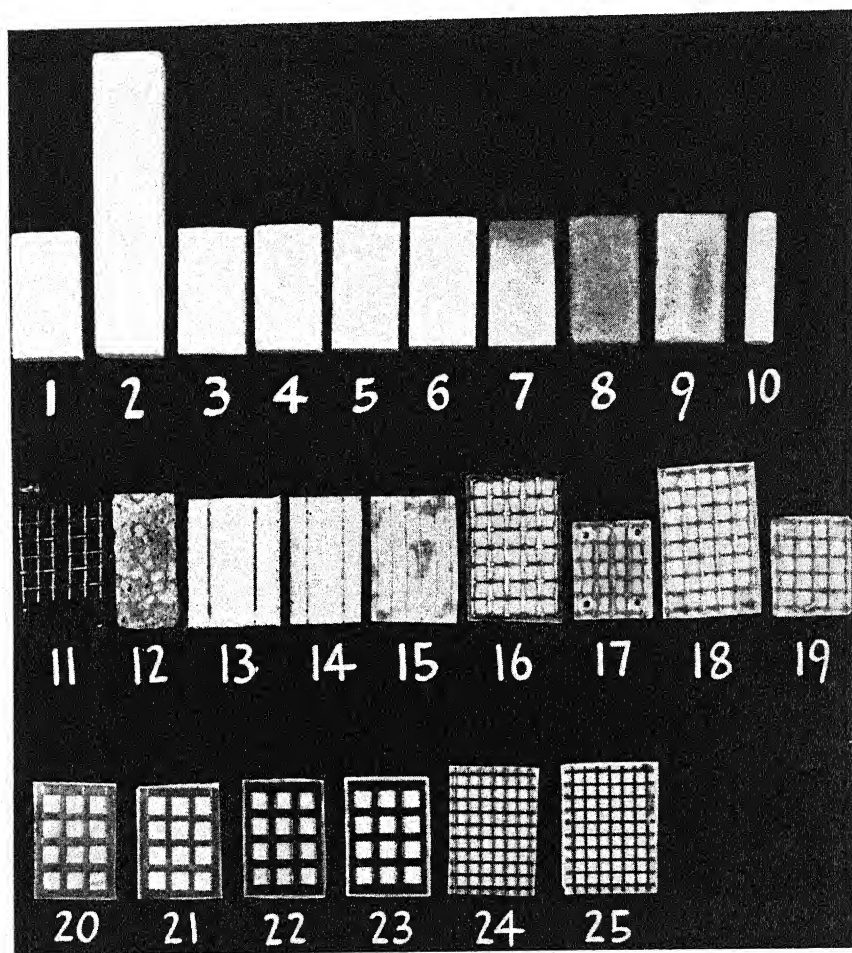


FIG. 1. SOME OF THE MANY DIFFERENT KINDS OF ABSORPTION UNITS STUDIED OVER A PERIOD OF 9 YEARS

1, 2, 3, plaster of paris; 4, hydrostone; 5, hydrocal; 6, dentalstone; 7, fired clay; 8, concrete; 9, sand-cement; 10, axial electrodes in plaster of paris; 11, contact electrodes; 12, cellulose sponge; 13, fiberglas, nickel wires woven into cloth; 14, nylon, nickel electrodes stitched into fabric; 15, nylon, triplicate electrodes woven in fabric; 16, 17, nylon, zinc-coated screen; 18, 19, fiberglas, zinc-coated screen; 20, nylon, zinc perforated plates; 21, fiberglas, zinc perforated plates; 22, nylon, stainless steel; 23, fiberglas, stainless steel; 24, nylon, nickel plates; 25 fiberglas, nickel plates.

have internal electrodes, and units 11 through 25 have external electrodes. The units with external electrodes were investigated with the hope that some simple design might be developed which would give satisfactory soil-moisture measure-



ments. The fabrics employed were nylon and fiberglass. In addition, rubber sponge, asbestos, and bare electrodes were also employed. The fabrics have been used in several ways, with the electrodes either in the form of wires stitched or woven into the woof and warp or in the form of perforated plates or hardware meshes enveloping and supporting the absorbent. Various kinds of electrode metals have been tested, including paladium, monel, copper, magnesium, stainless steel, pure nickel, and sterling.

The fabrics were cemented to the metal plates and then pressed.

#### DURABILITY OF ORGANIC AND INORGANIC MATERIALS

The so-called plastics, fibrous glass materials, sponge, and rubber absorbents first attracted attention because they are generally supposed to be relatively insoluble. Insolubility was considered desirable because it was thought to contribute to a greater durability within soil environments. But like "solubility," the term "durability" is only relative in meaning. No material has been found to last indefinitely in soil. Even fiberglass has a limited life under some soil conditions. A contributing factor is, of course, the large specific surface of those materials that are in a fine enough state of subdivision to provide the necessary pore-size distribution. In addition to the volume of circulating ground water to which a fiberglass unit is exposed, the reaction of the environment also determines its useful life. Alkaline conditions cause a more rapid disintegration than do acid environments. Nylon fabric was discovered to be more durable than fiberglass, although nylon is also slightly soluble in alkaline solutions.

So far as the useful life of an absorption unit is concerned, wire insulations may be more of a limiting factor than the absorbent itself. For most commercial rubber insulation, 5 or 6 years is the maximum expectancy. Even substances like vinylite, which is rated high in durability, cannot be expected to remain in satisfactory service for much longer periods.

It is thus seen that the useful life of an absorption unit imbedded in an average soil is subject to definite limitations because of the essentially dynamic characteristics of subsurface environments and the chemical activity of absorbent and insulation materials.

#### STANDARD FABRIC ABSORPTION UNIT

In the laboratory, most of the units with external electrodes shown in figure 1, especially unit 24, gave satisfactory measurements of soil moisture and therefore appeared very promising. Figure 2 shows the moisture curves obtained in the laboratory with unit 24 on 25 different soils. Like all other units with external electrodes, however, this unit, when buried in the ground, gave field results that had no very close relationship to the laboratory soil moisture calibration. This discrepancy was due, undoubtedly, to external factors in the soil, such as degree of compaction, texture, structure, salt content, and electrical lines of force.

In view of these difficulties, it was decided to resort to the principle of the plaster of paris block (2), wherein the electrodes are imbedded in the block in a constant environment, which minimizes the effects of external factors. It is this principle of internal electrodes, together with the buffering action of gypsum,

that is mainly responsible for the success of the plaster of paris block as a soil moisture measuring unit.

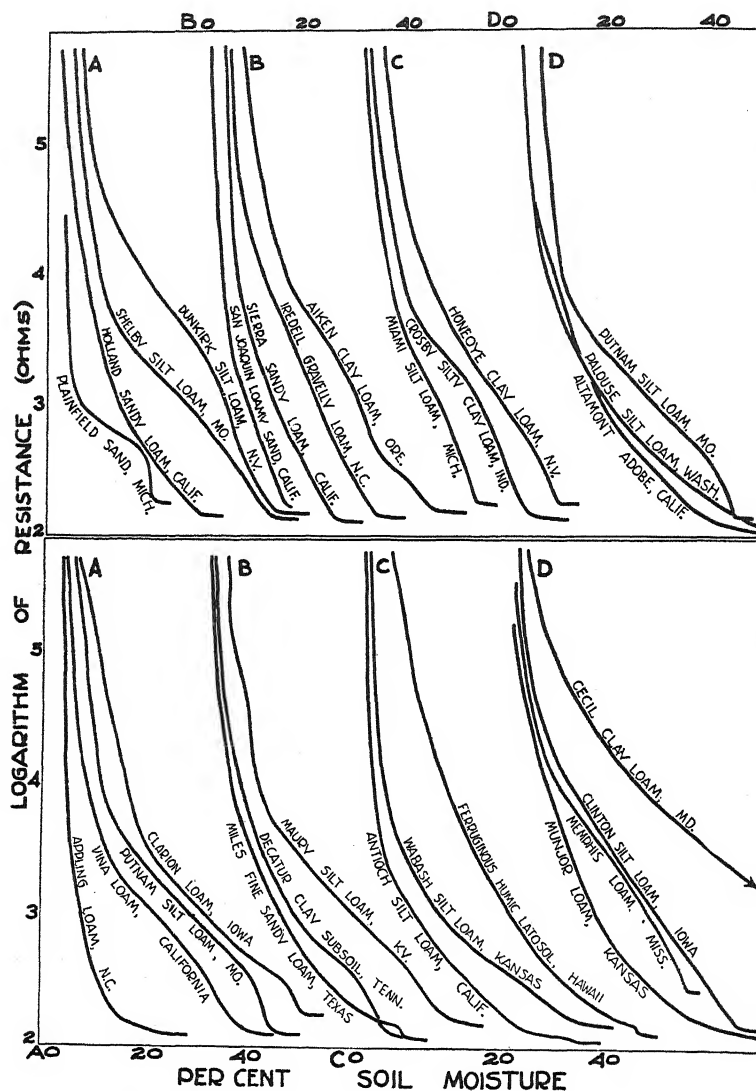


FIG. 2. MOISTURE CURVES OBTAINED WITH UNIT 24  
Letter beside each group of curves indicates the scale to which it is referred.

The final fabric unit developed (fig. 3) embodies the principle of the plaster of paris block. It consists of two perforated, extremely thin nickel plates, or two pieces of fine monel screen acting as electrodes, to which are silver-soldered wire leads. These electrodes are separated by wrappings of nylon or fiberglass fabric. The whole assemblage is then placed in a perforated nickel case, pressed under

high pressure, and the edges of the metal case are mechanically united to hold the enclosed assemblage together permanently. The enveloping case has  $\frac{2}{10}$ -inch square holes,  $\frac{1}{4}$ -inch centers straight, and is 64 per cent open. The holes cover the entire surface of the case, thus affording the absorbent a very large amount

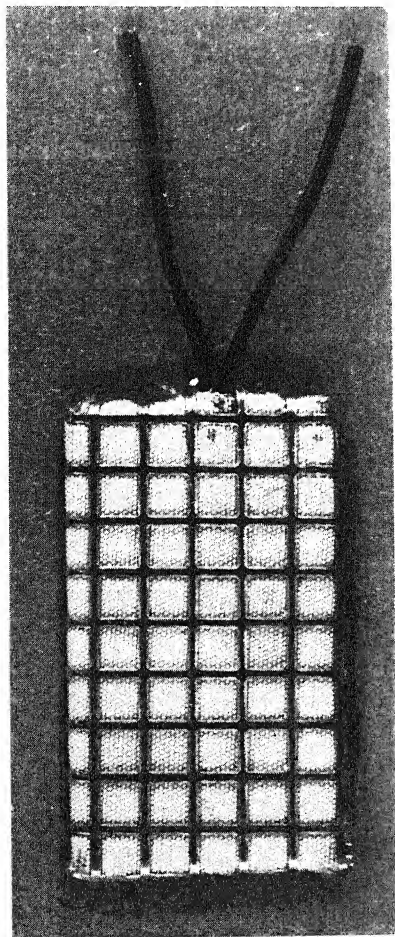


FIG. 3. STANDARD FABRIC ABSORPTION UNIT

This unit has internal electrodes and is based on principle of the plaster of paris block. Absorbent is fiberglass.

of exposure to the soil. Colman (7) has used a somewhat similar general design in his unit, which is also based on the plaster of paris block principle.

Both nylon and fiberglass were used in this unit as absorbents. In the laboratory, these fabric materials exhibited about the same absorbent characteristics. At present, fiberglass is preferred because it has much greater buffering action, which gives stability and accuracy to the performance of the units. The fiber-

glas used was in the form of a 2-inch tape specially made for this unit. It received no treatment except washing.

Nylon is stronger fabric and would probably last longer in the soil than fiberglass, but nylon is too inert and has virtually no buffering action.

As finally developed, the fabric absorption unit has performed satisfactorily in measuring soil moisture in the field. Compared with plaster of paris blocks, the fabric unit is superior in the following ways: 1. It measures the entire range of soil moisture from saturation to air-dryness; 2. It has very little lag in its response to moisture changes; and 3. It will last longer under extremely wet conditions.

Plaster of paris units, however, possess a unique advantage in that their external surfaces are uniformly absorbent. If only a small area of surface is in contact with the soil, a fair index of soil moisture is obtained. Compared with plaster of paris blocks, fabric units possess four inherent disadvantages: 1. The inert chemical characteristics of fabric absorbents makes them susceptible to changes in salt content in the soil solution, whereas plaster of paris, on the contrary, exhibits considerable buffer capacity with respect to changes in salt concentration; 2. The wrapping of fabric around the screen electrodes makes the contact artificial and imperfect, whereas in the gypsum block the electrodes are perfectly imbedded and set; 3. The outer metal case of the fabric unit tends to interfere with a perfect contact between soil and unit; and 4. Fiberglass may absorb salts or react chemically with some soils.

Fabric units are not intended, therefore, to replace plaster of paris blocks, which are well adapted to agronomic investigations. It is thought, however, that fabric units may supplement block installations, particularly in wet and saturated conditions. Engineers and hydrologists may find fabric units well adapted to purposes where an index of the entire soil moisture range is of interest.

Although their construction is somewhat complicated, fabric units, when uniformly made, give similar readings at similar moisture levels. Newly constructed units immersed in tap water show a variation of about 0 to 25 ohms in their initial resistance.

When fiberglass units are buried in the soil, the fiberglass is expected to dissolve gradually. When this takes place, the contact between absorbent and electrodes may possibly deteriorate, with a resultant change in calibration. To overcome this difficulty, the outer case of the unit is made of thin nickel, rather than very rigid metal, so that the pressure of the soil will help absorbent and electrode maintain good contact.

#### PRINCIPLE OF FABRIC MOISTURE-ABSORBENT UNITS

Like plaster of paris blocks, fabric units provide a continuous measure of field-moisture variations. These units are imbedded in the soil at desired depths and left there permanently. Soil moisture is determined by measuring the electrical resistance of the unit. Resistances are then translated into moisture percentages by means of previously determined calibration curves.

Both nylon and fiberglass fabrics seem to function on the same principle as

plaster of paris blocks. The electrical resistance of a fabric absorbent varies with its moisture content. When the surrounding soil is wet, unit resistances are low; as the soil dries, resistances increase. The magnitude of the resistance change depends on the physical and chemical characteristics of the absorbent material. Since the selected materials are good absorbents and good capillary conductors, an equilibrium is readily established between moisture in the fabric and moisture in the soil.

#### RESISTANCE-MEASURING INSTRUMENTS FOR FABRIC UNITS

A special Wheatstone bridge devised for measuring plaster of paris block resistances (5) is also suited to the fabric units. This instrument, as now manufactured, combines rugged, compact construction with a high degree of sensitivity. It is a completely self-contained unit, which is designed to measure resistances in circuits containing appreciable capacitance, such as is encountered in installations where the units may be connected by up to 200 feet of commercial multiple-strand, rubber-coated copper wires. The instrument will operate at temperatures considerably below freezing.

Making use of the sound characteristics of the necessary oscillating current, headphones have proved to be the most useful type of null indicator. In conjunction with the present circuit design, a great contrast in tone volume, which rapidly fades to a minimum level within an extremely narrow range, contributes to the ease of adjusting the instrument. For prolonged operation, sponge-rubber cushions over the phones have been found to be helpful by reducing the interference of extraneous sounds such as are produced by wind currents. They also distribute the mechanical pressure over the entire ear cartilage, which adds to the comfort of the operator. Because of the distinct and powerful signal provided by the circuit arrangement, readings are made without difficulty under adverse conditions such as noise and wind.

To avoid the influence of various capacitance factors present in field circuits, a large condenser has been included which contributes greatly in obtaining a good null balance within the bridge. The instrument is powered by dry cell batteries feeding through a 2,000-cycle electronic oscillator. An extremely wide range of sensitivity is obtained by inserting two series of standardized resistances in opposite arms of the bridge; the proper combination is selected by means of multiplier switches, and the final null point is obtained by adjusting a logarithmic potentiometric rheostat fitted with a 6-inch graduated dial. The bridge is thus adjusted to a null point by manipulating five dials in a matter of seconds. Null points are reduced to the width of not more than two turns of the rheostat coil, which permits finer adjustment than can be conveniently interpolated from the graduations.

Compared with general purpose conductivity bridges which are standard items of equipment in most research laboratories, this special bridge has several advantages: it is self-contained and portable; the power unit is rugged enough to withstand shocks encountered in field work; and a sharp null point is obtainable as a result of including the variable condenser in one of the bridge arms. Com-



pared with the special bridge originally designed for this work, the newer modification has a much wider range: 5,000,000 ohms as against 100,000 ohms for the old model. The oscillator has also been improved, the new model having a much higher power output at a frequency of 2,000 cycles. The high power output produces a loud signal that facilitates adjustment because of its great contrast with the null balance, which is, under most conditions, marked by total silence.

A more readily portable instrument in the form of an ohmeter based on the bridge circuit has also been developed. This meter is a direct reading type and somewhat easier to read than the Wheatstone bridge, but it is not so accurate an instrument as the bridge. It has been used for the last 3 years in greenhouse and irrigation studies. Its description and application will form the subject matter of a separate paper.

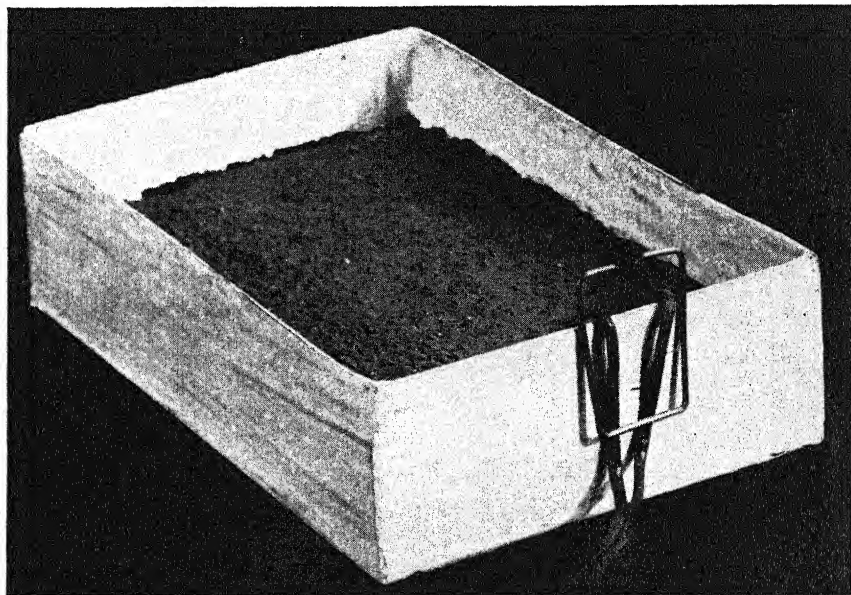


FIG. 4. INSULATED CALIBRATION PAN SHOWING FLEXIBLE LEADS FIRMLY CLIPPED IN PLACE

#### CALIBRATION OF FABRIC UNITS

For research investigations it is considered advisable to calibrate fabric absorption units for each soil installation.

A satisfactory calibration procedure consists of placing 25 gm. of sieved air-dry soil in the bottom of a small painted metal pan, 1 by 2 by 2 inches. On top of this leveled soil is placed the unit. To insure that it will remain in place and not disturb the sample in which it is imbedded, very thin, flexible leads are firmly clipped to the rim of the pan (fig. 4). Then another 25 gm. of the soil is placed over the unit. The pan is tapped horizontally and vertically to pack and level its contents. Water is gently added until the soil is saturated and a small quantity of excess water covers the surface.

Because the pan bottom is not perforated it does not allow drainage nor does it permit replaced air to escape. Sometimes air bubbles are trapped in the electrode grids, and as a result, the unit floats upward. This difficulty is remedied by gently pushing the unit down with a thin sheet of metal 2 inches wide, and gently tapping, which releases nearly all bubbles. In rewetting for subsequent drying cycles on the same sample, a similar procedure is followed. The unit is pushed down and lightly tapped after every addition of water. These precautions are vital for successful calibration in order to ensure adequate and uniform contact between soil and absorbing surfaces.

After wetting, the sample slowly dries under ordinary temperature and humidity conditions prevailing in the laboratory. At frequent intervals, depending on the drying rate, resistances are measured by means of the soil moisture bridge. For each resistance value a corresponding moisture value is obtained by weighing the entire pan, unit, and soil. A Toledo balance with a sensitivity of 0.50 gm. has proved convenient for this purpose. Moisture percentages are calculated from the net losses and the already determined oven-dry sample weight. Although some samples shrink and crack when approaching air-dryness, these structural changes do not appear to influence the accuracy of the calibration method, which is the most simple and rapid so far devised.

#### PERFORMANCE CHARACTERISTIC OF THE STANDARD FABRIC UNIT

Figure 5 presents typical moisture curves as obtained on four different soils by the standard fabric absorbent unit. As indicated, each soil was dried three times, and each curve is made up of points obtained from three successive drying cycles. It is apparent that fabric absorbent units tend to produce a somewhat irregular pattern of exhaustion curves, whereas the curve resulting from use of the gypsum blocks is a smoothly distributed pattern of the same type (5). Colman (7) has obtained a double-S-shaped pattern of moisture curve with his unit. This irregularity in the curve is caused by several factors, the most important of which are imperfect contact between the electrodes and the fabric absorbent, interference of the outer metal case with perfect contact between the soil and the unit, chemical and physical characteristics of the soil, and transition of the different forms of water. The most marked change in the curves takes place at about the permanent wilting point of soils. The curves reveal however, a satisfactory degree of sensitivity, accuracy, and reproducibility of results of the standard fabric unit. In addition, they show that fabric absorption units function over a wide range of soil moisture extending from saturation to air-dryness.

Saturated soil conditions are marked by constant low resistance values in the vicinity of 50 to 200 ohms resistance. As the excess water disappears and air begins to enter the soil pore-space, most curves are marked by a critical point, after which further losses are indicated by relatively large increases in resistance. As air-dry conditions are approached, the curves become asymptotic with respect to moisture content, generally in the vicinity of 1 million ohms.

The range of available moisture is marked at the minimum level by the wilting

percentage and at the upper limit by the field capacity. These moisture levels are not represented by the same resistance values in each soil. The wilting percentage of soils with average salt content appears to be around 10,000 to 15,000 ohms as determined by the fabric unit, in comparison to about 75,000 ohms as determined by the plaster of paris block.

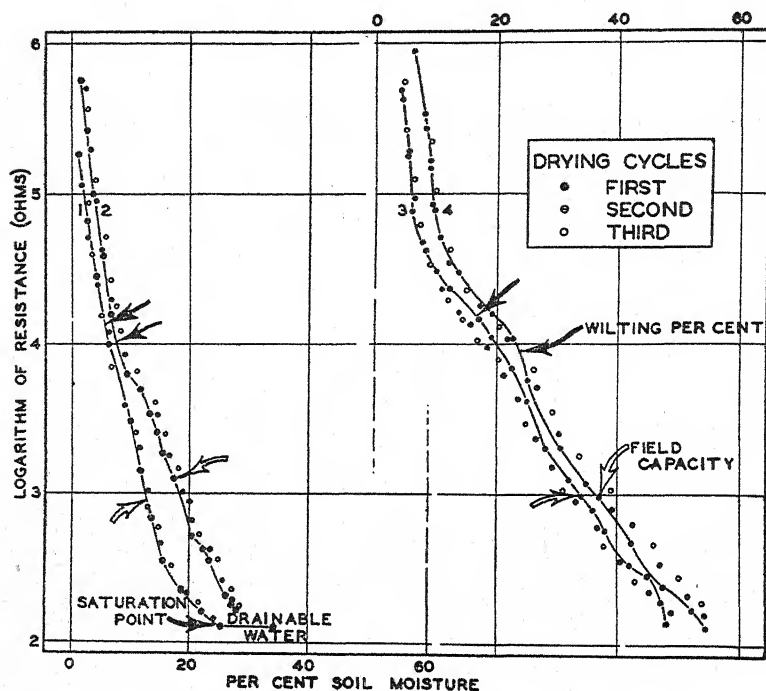


FIG. 5. SENSITIVITY, ACCURACY, AND REPRODUCIBILITY OF RESULTS OF THE STANDARD FABRIC ABSORPTION UNIT

Soil moisture curves of 1. San Joaquin loamy sand; 2. Miami silt loam; 3. Clinton silt loam; 4. Hawaiian clay.

#### EFFECT OF TEMPERATURE ON FABRIC UNITS

As with plaster of paris blocks, temperature influences the resistance of fabric units at any given moisture level. In figure 6 are plotted the temperature variations in the resistance of fabric units at three moisture levels. Though there appears to be considerable variation in resistance over this entire range of temperature, the effect of changes between 70° and 90° F. is nearly negligible. At low moisture levels, for example, the error in terms of soil moisture percentages is about  $\pm 1\frac{1}{2}$ . At a moderate moisture content, where this particular curve flattens out, the error is greater, but even here it does not exceed  $\pm \frac{3}{4}$  per cent.

From this evidence it is concluded that for practical purposes, such as irrigation control, the influence of changes in temperature on soil moisture-unit resistance relationships can be ignored. For research investigations, however, it may be

necessary to correct resistance readings to a constant temperature. Figure 7 shows a method for making approximate temperature corrections.

Although the common liquid expansion type of thermometer can be used to measure surface soil temperatures, three other types have been found more con-

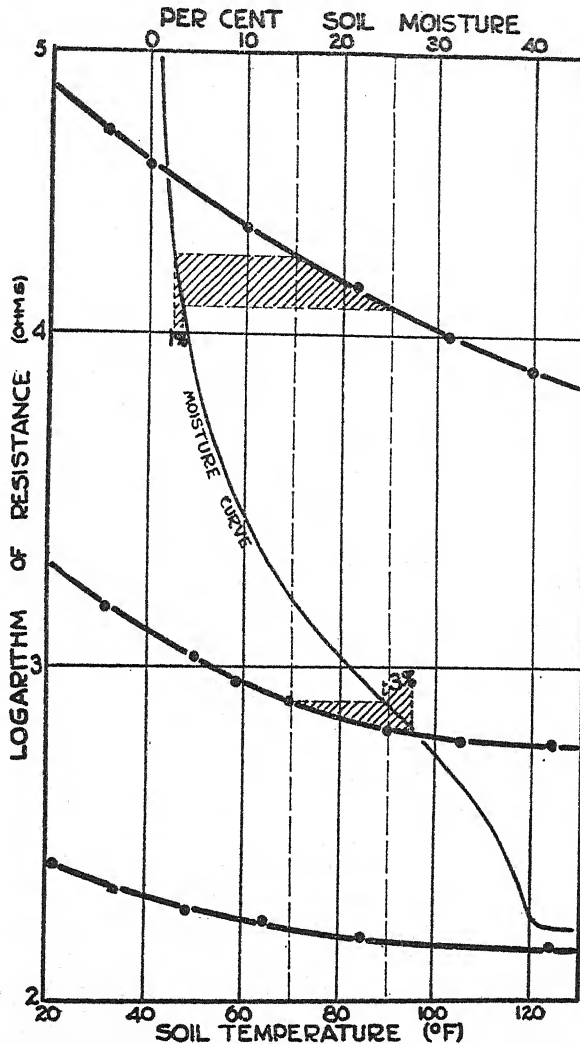


FIG. 6. INFLUENCE OF TEMPERATURE ON RESISTANCE OF FABRIC UNITS

venient for field use. Liquid electrical resistance thermometers (4) and thermistors manufactured by the Western Electric Company are well adapted to deep installations. Both of these resistance thermometers are especially convenient because their resistance range falls within that of the Wheatstone bridge used to measure unit resistances. A bimetallic dial-indicating instrument offered



by the Weston Company is useful for measuring temperatures at shallow depths and is much more rugged than conventional glass-stem thermometers.

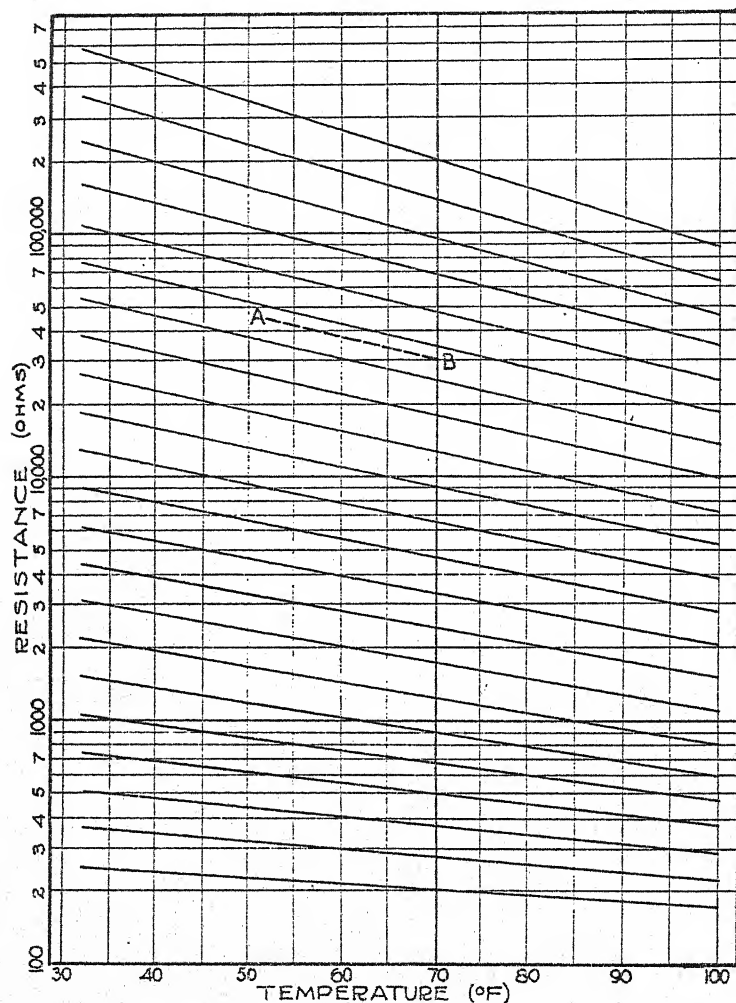


FIG. 7. TEMPERATURE CORRECTION FOR FABRIC ABSORPTION UNITS

A resistance reading of 45,000 ohms at 52°F. at point A represents a resistance of 30,000 ohms at 70°F. at point B.

#### EFFECT OF SALT CONCENTRATIONS ON FABRIC UNITS

A major advantage of plaster of paris units is that the chemical characteristics of soil materials normally encountered in humid regions are dominated by the chemical characteristics of the absorbent itself. Although the salt contents of most soils differ, and although there are variations in the salt contents of a single sample from one drying cycle to another, the normal solubility of the block and the salt content of the solution immediately around the electrodes remain fairly



constant. Changes in the salt content of the soil solution are therefore less clearly reflected in the resistance of an imbedded plaster of paris unit, which indicates mainly changes in the moisture content of its environment. This resistance to a change in salt concentration exhibited by plaster of paris has been termed *buffering*.

It has already been pointed out that fabric absorbents of the nylon and fiberglass type are more inert than plaster of paris and do not exhibit such marked buffering capabilities. This is especially true of nylon, which has very little buffering action. Fiberglass, on the other hand, exhibits a surprisingly high relative degree of buffering action, and errors caused by variations in salt content in the soil are probably not so great as might be expected.

A dominant effect of large salt content in the soil is to make the fabric unit less sensitive to moisture changes and to limit the sensitive resistance range of the fabric unit.

#### AGRONOMIC AND HYDROLOGIC APPLICATIONS OF FABRIC UNITS

These units have been tested under field conditions and have been found to function satisfactorily. Plant roots do not penetrate the absorbent fabric, nor do they interfere with the soil moisture-resistance relationship.

As previously pointed out, the wilting point of field soils with average salt content is approximately 10,000 to 15,000 ohms as determined by fabric units. Soils containing larger quantities of salts give lower resistance values at the wilting point, depending on the quantity of salts present.

When field soils contain about 50 per cent of their available water, the resistance displayed by an imbedded fabric unit is about 5,000 ohms for soils with normal salt content and less than 5,000 ohms for soils with larger salt content.

In special agricultural enterprises which depend on irrigation practices, fabric units imbedded in the zone of maximum root development furnish a guide to the proper time to add water (fig. 8). In soils with normal salt content, for example, water might be added when resistances exceed 5,000 ohms. In soils with higher salt content, it might prove advisable to add water when resistances exceed the range of 3,000 to 5,000 ohms. At these resistance levels, about 50 per cent available water remains in the soil.

As with plaster of paris blocks, freezing within the soil is indicated by increasing resistances. Initially, freezing of soil water produces a curve similar to a drying curve. As long as unfrozen water remains in the unit, however, a fairly high conductivity is maintained. When all water has been frozen, so that none exists as a liquid, the unit resistance rises abruptly. Freezing does not destroy the absorbent, nor does it appear to have any bad effects on the subsequent functioning of a fabric absorbent.

#### DIRECTIONS FOR USING FABRIC UNITS

For the most accurate determination of soil moisture, fabric units must be calibrated for each soil, and temperature corrections applied to each measure-

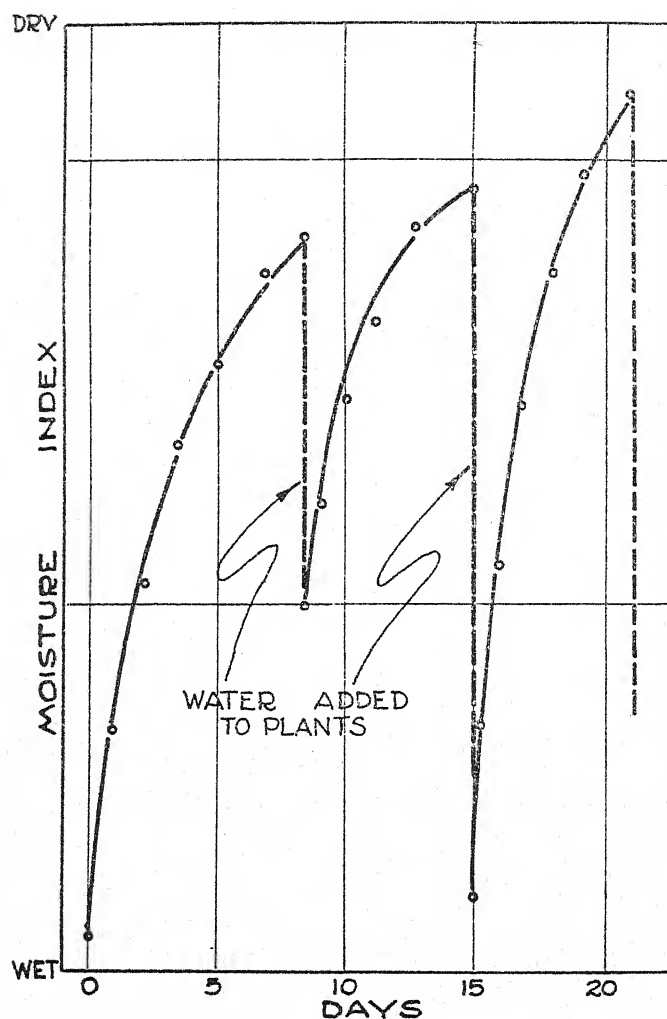


FIG. 8. MOISTURE CYCLES IN A SOIL SUPPORTING RYE  
Moisture index is ohms resistance indicated by fabric absorption unit.

ment. Although directions for calibration have already been discussed, it is here emphasized that the following points must be closely observed:

1. An excess of water must be added to the soil when the units are calibrated. Not only must the sample be saturated, but there must be a thin film of excess water on top. This precaution ensures an intimate contact between soil and absorbent surfaces.
2. Air trapped underneath the unit must be expelled by gentle pressure on the unit and by tapping the pan.
3. After the units have been properly settled in the pan and water has been added, the pan is covered and allowed to stand for 5 to 10 hours to allow chemical and physical equilibriums to become established.

4. For calibration purposes, fabric units should be equipped with flexible lead wires so that handling after equilibrium is established will not disturb the absorption unit or the sample. Clamping the leads to the pan assures that the unit will not be disturbed during subsequent manipulations.

5. It is recommended that calibration measurements be made on a second, rather than the first, drying cycle. After every wetting, however, the air must be expelled from under the unit and the pan contents settled by gentle tapping.

6. Drying should not be hastened, but should be allowed to take place slowly.

When units are installed in the field, a 4-inch post-hole digger is employed. Small samples of various horizons are set aside for calibration purposes. At desired depths the bottom of the hole is stamped flat and a unit, placed horizontally, is well firmed within the material of that particular horizon. It is advisable to place some loose soil on top of the tamped bottom before setting the units. This will ensure a better contact at the bottom. Then a small amount of soil is placed on the top of the units and firmly tamped. This procedure is employed for every unit buried in the same hole.

#### SUMMARY

A fabric absorption unit for making an electrical resistance measurement of the complete range of soil moisture from saturation to air-dryness is described. This unit has internal electrodes and was made on the same principle as the plaster of paris block previously described. The absorbent is either nylon or fiberglas.

Fabric units are not intended to replace plaster of paris blocks. Because fabric units operate, however, over a wide range of soil moisture, it is thought they may be of some interest to engineers and hydrologists who are interested in following moisture trends from air-dryness through saturation. In agronomic problems, fabric units may supplement plaster of paris blocks in wet and saturated conditions where the latter do not function satisfactorily.

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# EFFECT OF VOLATILE DISINFECTANTS ON SURVIVAL OF MICROFLORA IN SOIL<sup>1</sup>

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A large amount of work has been done on the effect of "partial sterilization" of soil microflora (8). Comparatively little work has been done on effecting complete sterilization of soil. Steam sterilization is effective in achieving sterility, but it also changes soil properties, especially those related to soil organic matter. A few investigators have reported on the use of volatile disinfectants for complete sterilization, but none have studied the comparative efficiency of the disinfectants or the survival rates of the soil microflora. Roberts *et al.* (7), in a preliminary report, found that the use of ethylene oxide resulted in sterility and that soluble salts were not increased. Katznelson (5) sterilized soil by autoclaving for reinoculation studies.

The following investigations were undertaken to provide a method for sterilizing soil for laboratory studies, which would permit subsequent removal of the sterilizing agent and would cause a minimum of change in the soil itself. It was believed that the fumes of volatile disinfectants would best serve these purposes. A method was devised for storing soil in sealed containers with the atmosphere saturated with the fumes. It was believed that by first evacuating the system, contact with the disinfectant could be made even in the capillary pore space.

## PROCEDURE

A hole large enough for a No. 5 rubber stopper was cut through the screw lid of a quart jar, and a small wire basket large enough to hold a 20-ml. beaker was soldered to the underside of the lid beneath the hole. Two glass tubes were inserted through the rubber stopper so that a vacuum could be drawn through one and liquid could be transported through the other into the 20-ml. beaker. One hundred fifty grams of soil (Merrimac sandy loam, moisture content 25 per cent) was placed in the bottom of the jar, the lid was sealed with plastic clay, and a vacuum (40 mm. Hg) was drawn through one of the tubes. About 10 ml. of the disinfectant to be tested was drawn into the beaker through one of the tubes by carefully opening a screw clamp on the other of the glass tubes, and the vents were then closed again.

At the indicated intervals, the jar was opened and the lid replaced with an ordinary one. The soil was thoroughly mixed by rotating the jar, and samples of the soil were removed aseptically for plate counts. Samples for determinations of ammonium acetate-soluble copper and manganese were taken at the end of each experiment.

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This technique was modified slightly when HCN was studied. When water was drawn into the beaker containing calcium cyanide, it was difficult to prevent the powder from being blown into the soil. This difficulty was overcome by

TABLE 1

*Effect of chloroform and hydrogen cyanide on survival of soil microflora in Merrimac sandy loam*

DAYS EXPOSED	SURVIVING MICROFLORA,* IN THOUSANDS PER GRAM OF SOIL	
	Chloroform	Hydrogen cyanide
0	7250 $\pm$ 1500†	7250 $\pm$ 1500
1	...	4300‡
2	...	3000
3	1000 $\pm$ 200	3600
4	...	2000
5	...	1800
6	1300 $\pm$ 400	1700
7	...	1400
8	800 $\pm$ 250	1800
9	...	...
10	80 $\pm$ 30	...

\* No attempt was made to differentiate between molds, actinomycetes, and bacteria.

† Average variation from the mean value of counts from five plates.

‡ These counts were made on single plates for a preliminary run.

TABLE 2

*Effect of chloropicrin, formaldehyde, and ethylene oxide on survival of soil microflora in Merrimac sandy loam*

DAYS EXPOSED	SURVIVING MICROFLORA,* IN THOUSANDS PER GRAM OF SOIL					
	Chloropicrin		Formaldehyde		Ethylene oxide	
	1	2	1	2	1	2
0	7250 $\pm$ 1500†		7250 $\pm$ 1520		7250 $\pm$ 1500	
1	402 $\pm$ 14	377 $\pm$ 39	284 $\pm$ 108	208 $\pm$ 38	0	0
2	348 $\pm$ 39	357 $\pm$ 12.8	2 $\pm$ 0.6	4 $\pm$ 1.8	0	0
3	155 $\pm$ 9	150 $\pm$ 14.2	0	0	0	0
4	99 $\pm$ 11	84 $\pm$ 17.5	0	0	0	0
5	32 $\pm$ 3	28 $\pm$ 6.4	0	0	...	...
6	6 $\pm$ 2.4	4 $\pm$ 3.2	0	0	...	...
7	0	0	0	0	...	...
8	0	0	0	0	...	...

\* No attempt was made to differentiate between molds, actinomycetes, and bacteria.

† Average variation from the mean value of counts from five plates.

enclosing the calcium cyanide in a gelatin capsule, which was placed in the beaker. A few milliliters of hot water drawn into the beaker served to melt the gelatin and react with the salt to liberate HCN.

Copper and manganese were chosen as indicators of effects of the disinfectants on the soil itself because they form, in soil, metallo-organic complexes (2) which

are readily decomposed. Soil manganese is also a sensitive indicator of the state of reduction. Copper was determined by the diethyldithiocarbamate method as described by Hurwitz (4), and manganese was determined according to Peech's periodate method (6). Digestion of the soil extract was carried out

TABLE 3

*Effect of hydrogen cyanide, chloropicrin, and formaldehyde on survival of soil microflora in Merrimac sandy loam*

Broth culture test

DAYS EXPOSED	HYDROGEN CYANIDE 1	CHLOROPICRIN 1 AND 2	FORMALDEHYDE 1 AND 2
1	+	+	+
2	+	+	+
3	+	+	—
4	+	+	—
5	+	+	—
6	+	+	—
7	+	+	—
8	+	—	—
9	+	—	...
10	+	—	...

TABLE 4

*Effect of ethylene oxide on survival of soil microflora in Merrimac sandy loam*

HOURS EXPOSED	SURVIVING MICROFLORA, IN THOUSANDS PER GRAM SOIL		BROTH CULTURE TEST	
	1	2	1	2
0	7250 $\pm$ 1500	7250 $\pm$ 1500	+	+
1	16 $\pm$ 1.8	8 $\pm$ 0.8	+	+
2	...	...	+	+
3	...	...	+	+
4	8 $\pm$ 7.0	10 $\pm$ 0	+	+
5	...	...	+	+
6	...	...	+	+
7	10 $\pm$ 6.6	7 $\pm$ 5.6	+	+
8	...	...	+	+
9	...	...	—	+
10	36 $\pm$ 11.3	10 $\pm$ 0	+	+
11	...	...	—	—
12	...	...	—	—
13	0	0	—	—

with a 1:1 mixture of perchloric and nitric acids after predigestion with  $\text{HNO}_3$ . The oxidized salts were then evaporated to dryness with 1:1  $\text{HCl}$  to convert difficultly soluble oxides, and the salts were dissolved in hot, dilute  $\text{HNO}_3$ . All reagents, where possible, were purified by redistillation from pyrex or by diethizone extraction. Blanks on the reagents were never large enough to necessitate correction.

Plate counts were made in quintuplet from duplicate jars after preliminary studies indicated the proper dilutions to be used. The culture medium used was soil extract agar containing 0.01 per cent of yeast extract with no other

TABLE 5  
*Effect of vacuum on the survival of soil microflora in Merrimac sandy loam*  
Soil incubated under 40 mm. Hg pressure

DAYS EXPOSED	SURVIVING MICROFLORA, IN THOUSANDS PER GRAM OF SOIL	
	Aerobic incubation	40 mm. Hg pressure incubation
0	7250 $\pm$ 1500*	7250 $\pm$ 1500
1	7000 $\pm$ 1200	4900 $\pm$ 1000
2	5600 $\pm$ 200	3600 $\pm$ 400
3	5300 $\pm$ 400	4100 $\pm$ 200
4	5300 $\pm$ 700	4300 $\pm$ 500
5	3900 $\pm$ 600	3600 $\pm$ 400
6	4500 $\pm$ 900	4100 $\pm$ 500
7	5800 $\pm$ 1000	6800 $\pm$ 500
8	7300 $\pm$ 700	5100 $\pm$ 400
9	12100 $\pm$ 1800	2900 $\pm$ 700
10	8900 $\pm$ 1000	5900 $\pm$ 500

\* Average variation from the mean value of counts from three plates.

TABLE 6  
*Effect of volatile disinfectants and heat on ammonium acetate-soluble copper and manganese in Merrimac sandy loam*

TREATMENT	MICROGRAMS PER 10.0 GM. DRY SOIL			
	Copper		Manganese	
	1	2	1	2
Untreated.....	26.5	24.9	1.4	1.4
Flowing steam, 10 minutes.....	29.3	30.2	16.0	15.4
Flowing steam, 30 minutes.....	29.0	32.8	38.7	40.0
Flowing steam, 60 minutes.....	29.8	24.1	65.5	69.0
Formaldehyde.....	55.6	40.3	94.0	76.5
Chloropicrin.....	91.4	126.8	185.5	216.5
Ethylene oxide.....	79.4		25.4	
Hydrogen cyanide.....	*		14.0	

\* Color too intense to be measured because of probable iron interference in determination.

carbon or nitrogen source added. An added check on sterility was made by adding about 2 gm. of the soil to nutrient broth. No growth after 48 hours' incubation was considered proof of sterility.

#### RESULTS

Tables 1, 2, 3, and 4 show the plate counts and broth culture tests of soil microflora surviving exposure to the disinfectants. According to the plate counts,

chloroform and HCN did not sterilize the soil after contact for 10 and 8 days respectively, whereas chloropicrin sterilized the soil after 7 days, formaldehyde after 3 days, and ethylene oxide after 11 hours. Broth culture tests confirmed these results, except that chloropicrin was shown to require 8 days for sterility.

The effect of lowered atmospheric pressure (40 mm. Hg) on the numbers of microorganisms was determined to discover whether the decrease in numbers was also affected by the decrease in oxygen tension. The same procedure was used except that no disinfectant was added to the jar. After dilutions were made and the plates were poured, one set was incubated at 40 mm. Hg pressure, the other set being incubated aerobically. The results are shown in table 5. Although some fluctuation of numbers occurred, no significant decrease was observed.

The effect of the treatments on the extractable copper and manganese contents are shown in table 6. Values for the effects of flowing steam are included for comparison. Here again, ethylene oxide proved superior in that only relatively slight increases in copper and manganese contents were noted. Formaldehyde and, especially, chloropicrin, two fumigants widely used in seedbed preparation, caused great increases in the extractable manganese content of the soil.

Ethylene oxide appeared to affect the solubility of the soil organic matter more than the other treatments, since the filtrate after extraction with ammonium acetate was slightly more yellow in color. Roberts *et al.* (7) postulated the formation of ethylene glycol in soil treated with ethylene oxide.

#### DISCUSSION

Ethylene oxide was found to be superior to the other disinfectants tested, both in its lethal qualities and in the relatively smaller changes induced in the soil as measured by increases in ammonium acetate-soluble copper and manganese. This method of sterilization of soil should prove to be valuable in laboratory studies of interactions of the soil microflora and plants.

Of practical interest are the results with hydrogen cyanide, formaldehyde, and chloropicrin, all of which have been extensively used in seedbed preparation and greenhouse soil treatment. On the basis of this work, hydrogen cyanide is of questionable value as a sterilizing agent since, after 8 days' exposure, the numbers of soil microflora were not greatly reduced. Under field conditions, it is doubtful whether the gas would remain in high enough concentration for even that length of time. Chloropicrin, which sterilized the soil after 8 days' exposure, may also be of questionable value from this point of view.

The increase of the ammonium acetate-soluble manganese and copper when the soil was treated with chloropicrin and formaldehyde was large enough to warrant further investigation into possible toxic effects resulting from these treatments. Concentrations of 1 to 5 p.p.m. of copper (3, 4) and 15 p.p.m. of manganese (1) have been reported as being toxic to plants. The extractable concentrations resulting from treatment of soil with fumes of chloropicrin were 10.9 p.p.m. of copper and 20.1 p.p.m. of manganese.

## SUMMARY

The effects of chloroform, HCN, formaldehyde, chloropicrin, and ethylene oxide on the survival of soil microflora in an evacuated system were determined. The effect of these disinfectants on the solubility of soil copper and manganese in ammonium acetate was also shown. Ethylene oxide sterilized soil after 11 hours' exposure, formaldehyde after 3 days, and chloropicrin after 8 days. Chloroform and HCN decreased the numbers of viable microorganisms but did not sterilize soil after 10 and 8 days' exposure, respectively. Of the three effective soil sterilizing agents found, ethylene oxide was the most lethal under the conditions used and resulted in the least increase of ammonium acetate-soluble manganese. Possibly toxic concentrations of copper and manganese resulted from the use of chloropicrin.

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## BOOKS

*The Chemical Formulary.* Edited by H. BENNETT. Chemical Publishing Co., Inc., Brooklyn, New York, 1948. Pp. 448. Price \$7.

This is the eighth volume of the Chemical Formulary. It does not replace the previous volumes but is a supplement to them. The entire field of chemistry and its applications is broken up into 22 units, of which farm and garden preparations, food products, insecticides, fungicides, and weed killers are of most interest to agriculture. But most readers will find much of value in the discussions of adhesives, cosmetics, drugs, emulsions, inks, lubricants, construction materials, metals, paints, paper, photography, plastics, polishes, explosives, soaps, and textiles as well. The index contains weights and measures with conversion charts, a list of over 1000 trade-name chemicals, and the names of 1209 sellers of chemicals and supplies. Everyone who picks up the volume will find something of value to him in his work.

*Farming and Democracy.* By A. WHITNEY GRISWOLD. Harcourt, Brace and Company, New York, 1948. Pp. 227. Price \$3.

The outcome of a fellowship award made to the author by the John Simon Guggenheim Memorial Foundation, this book deals with the "family farm" as a mainstay of democracy. This concept is tested by an examination of the agriculture of Great Britain, France, and the United States. The author concludes that the concept is outmoded in that the family farm is often an uneconomic unit. In his opinion, British democracy made its most rapid progress after the family farm had largely disappeared. France provides the best example of the family farm concept in that holdings in that country have been divided and subdivided by inheritance until their operation with modern machinery is virtually impossible. The book is a very timely one and merits careful reading by all those who have to do with planning the future of American agriculture.

*Our Plundered Planet.* By FAIRFIELD OSBORN. Little, Brown and Co., Boston, 1948. Pp. 217. Price \$2.50.

This book is dedicated "to all who care about tomorrow." The author has the conviction that we are rushing forward unthinkingly "through days of incredible accomplishment, of glory, and of tragedy" but that we have forgotten that we are dependent upon the soil as our source of life. He points out that our pattern of land use has been to "cut, burn, plant, destroy, move on," and that the United States, during the last century, has been more violent and destructive of forest, grassland, wildlife, and water resources than any other country that has yet come into existence. The author thinks the situation can be improved only as more people come to realize that the discord among nations is traceable to diminishing productivity of soils and to increasing population pressures. The more important chapters deal with the long view; man—the new geologic force; Asia—then and now; Mediterranean lands and Africa; Russia,

Europe, and Australia; and the New World. A comprehensive bibliography and reading list of some 130 items is appended. The book provides important and stimulating reading.

*Rothamsted Experimental Station Report for 1946.* Rothamsted Experimental Station, Harpenden, England, 1948. Pp. 114. Price 3/-.

This report gives a brief account of the activities of each of the several technical departments. Among the more interesting researches discussed are those dealing with deep plowing, slow drainage, clay studies, evaporation, bulky organic manures, fertilizer placement, basic calcium phosphate, manganese, mycorrhiza, bacteriophage, selective destruction of bacteria, molybdenum, physiology of leaf growth, experimental design, virus diseases, take-all disease of wheat and barley, pyrophosphate as an organic-matter extractant, garden slugs, foul brood, effects of D.D.T., and reports on long-time field experiments. The appendix contains a list of 31 publications, with abstracts of most of them.

*The Spectrographic Analysis of Soils, Plants, and Related Materials.* By R. L. MITCHELL. Commonwealth Bureau of Soil Science, Harpenden, England, 1948. Pp. 183, figs. 23. Price 12/6.

This is Technical Communication No. 44 of the Commonwealth Bureau of Soil Science, in board covers. Its purpose is to review the literature on spectrographic methods of analysis in relation to their possible use in the field of agriculture and to present some of the methods that have been developed over a 12-year period at the Macaulay Institute of Soil Research. The main chapters in the publication deal with the emission of spectral lines, the photographic plate, flame emission, arc, and spark methods, notes on individual elements, preparation of samples, and suggestions on application to the agricultural field. A bibliography of over 800 papers is appended, as is also a cathode layer arc spectrogram of a mineral sample on which the more important trace-constituent lines are indicated. The publication is a highly important contribution to the literature in this field. It will be of special interest to those concerned with the use of the spectrograph for the examination of plants and soils.

*Works of French Agronomic Stations Between 1939 and 1945.* Ministère de l'Agriculture, Paris, 1947. Pp. 159.

The subject matter of this report, presented in both French and English, is divided into methods and techniques, soil fertilization, production and improvement of crops, and miscellaneous items. The report lists all the publications of the several stations and gives fairly good abstracts of the most important ones. It provides a good review of the progress made during the war years. For the graduate student who needs practice in reading and understanding the French language, the volume should prove especially useful.

THE EDITORS.

# MODIFICATION OF GRAHAM'S METHOD FOR DETERMINING SOIL ORGANIC MATTER BY COLORIMETRIC ANALYSIS

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Walkley and Black (3) have developed a method for determining soil organic matter in which the sample is subjected to wet oxidation by chromic acid and sulfuric acid, the excess chromate being then titrated with ferrous sulfate. A rapid alternative method, adopted by Graham (2), is to measure the yellow color of the excess (unreduced) chromate, or to measure the green color of the oxidized reagent. Barton and Prutton (1) have also used this method to determine hemicellulose in an artificial silk factory.

Experiments by the author and his associates have shown that measurement of the yellow color is a suitable method and that the amount of carbon oxidized can be calculated without the necessity of calibrating the color charts by means of the dry combustion method. A "recovery" factor can be applied to express the results in terms of percentage organic matter in soil. Graham leaves the oxidized diluted mixture stand for about 5 hours to remove turbidity. This slows down the work and, if many samples have to be tested, a large number of flasks are in use at the one time. Only one batch can be analyzed in a working day. In addition, it was found in this laboratory that turbidity was not completely removed by this procedure. The obvious remedy was to filter the solutions through paper. By this expedient a batch of 10 soils can be tested in about 1 hour. Barton and Prutton (1) mentioned that dilution initiates a slow color change, which, however, is virtually complete in 30 minutes. The author has also found that the reading which is made about 30 minutes after dilution (since cooling and filtering occupy about that time) does not change after 5 hours' further standing.

## MODIFIED METHOD

Weigh on a square of glazed paper 1 gm. or  $\frac{1}{2}$  gm., according to organic matter content expected, of air-dry soil passing through a sieve with 2-mm. round holes and transfer it by a camel's-hair brush to a 250-ml. pyrex conical flask. Add 10 ml. of  $N K_2Cr_2O_7$ . If only the green color has to be determined, the reagent can be made from commercial dichromate roughly weighed; otherwise, use analytical reagent quality, accurately normal. Add rapidly 20 ml.  $H_2SO_4$ , 98-99 per cent. Swirl quickly for 10 seconds and allow the flask to stand on asbestos or a wood surface for 10 minutes or a little longer. Add 100 ml. water. Cool in a water bath to room temperature. Filter through Whatman No. 1 or similar paper, rejecting the first 20 ml. Measure the green color, using a red or orange

<sup>1</sup> The writer thanks the directors of the Irish Sugar Co., Ltd., for permission to publish this paper.

filter. A suitable range of readings on the "Spekker" absorptiometer was obtained by using 4-cm. cells. These are most conveniently emptied by inserting a tube connected to the vacuum line. Further dilution (10 ml. to 50 ml.) was found necessary to get a suitable range of readings of the yellow color. A violet filter and 1-cm. cells were used.

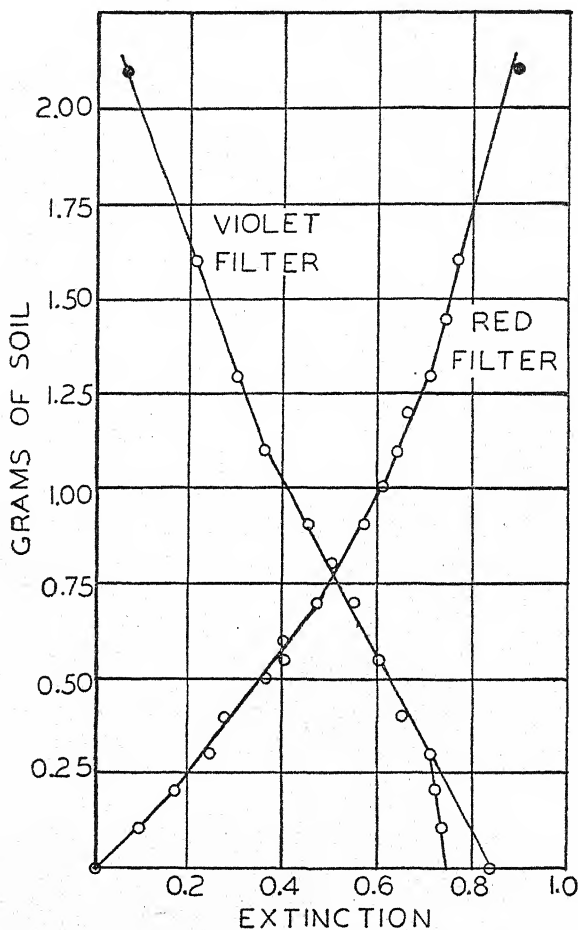


FIG. 1. READINGS OF SPEKKER ABSORPTIOMETER ON VARIOUS WEIGHTS OF THE SAME SOIL SAMPLE

#### EXPERIMENTAL RESULTS

To obtain the relationship between color and organic matter, a sample of soil was sifted through a 30-mesh screen so that small portions could be weighed without errors due to segregation. Various weights were treated with the reagents, and the results are shown graphically in figure 1.

Three completely reduced solutions were prepared by taking 10 ml.  $K_2Cr_2O_7$  reagent with excess (about 1 gm.) of solid potassium metabisulfite and treating



the solution with  $\text{H}_2\text{SO}_4$  and water as in the soil tests. Extinction values were 0.87, 0.91, and 0.91 with red filters and 0.06, 0.04, and 0.08 with violet filters. Another completely reduced solution was prepared by taking some of the filtered solution from the test with 1.6 gm. of soil and adding a crystal of metabisulfite, which was allowed to dissolve. Extinction values of 0.90 with red and 0.05 with violet filters were obtained. Average figures for extinction of 0.90 and 0.06 respectively have therefore been accepted for a fully reduced solution.

It can be seen that the increase of green color is, in fact, accompanied by a proportionate decrease of the yellow color. In the tests using small quantities (0.1 and 0.2 gm.) of soil the results are anomalous, the points being off the main line (graph for violet filter). Walkley (4) pointed out that the thermal decomposition of chromic acid is catalyzed by ignited soil, and therefore also probably by unignited soil free of organic matter. The color of the dichromate solution prepared without soil is the same irrespective of whether  $\text{H}_2\text{SO}_4$  is added before or after dilution with  $\text{H}_2\text{O}$ . As much more heat is developed with the former procedure, it appears that there is no thermal decomposition except when soil is present. With 0.5- to 1.0-gm. samples the readings give virtually a straight-line graph which, when produced, passes through the point, 0.84 Spekker reading, corresponding to the color of unreduced dichromate.

The solid circles at the tops of the curves in figure 1 represent the average colors of the totally reduced solution. Their exact position in respect to the ordinate is uncertain because extrapolation is very difficult in the case of such steep curves. Obviously, however, they are at least approximately in line, which shows that the yellow and green colors of the dichromate and chromium ions respectively can both be measured without serious interference from the colors of soil substances.

Because of the aforementioned difficulty of extrapolation, the curves were calibrated in terms of organic matter, as follows: Solutions of dichromate containing different amounts of normal solution made to 10 ml. were treated with sulfuric acid and water as in the soil test. To the color readings obtained, was added a correction for the color absorption which would occur if the solution also contained reduced dichromate equivalent to the difference between 10 ml. and the quantity used. The correction is, of course, based on the figure 0.06 for 10 ml. of totally reduced dichromate and *pro rata*. The results are shown in table 1.

Ten milliliters of dichromate is stoichiometrically equivalent to 0.03 gm. carbon or 0.0518 gm. organic matter (since soil organic matter contains about 58 per cent carbon). The room temperature was between 18 and 21°C. in all tests, and a recovery factor of 77 per cent (average) is assumed under these conditions (3), corresponding to 6.7 per cent organic matter if 1 gm. of soil is used.

From figure 1 the color 0.66 should correspond to  $0.067 \times 10 = 0.0134$  gm. organic matter in 0.4 gm. soil, or 3.35 per cent. Similarly the color 0.41 is equivalent to  $0.067 \times \frac{1}{2} = 0.0335$  in 0.98 gm., or 3.42 per cent. By rounding off the average to 3.4 per cent, the organic matter corresponding to the various weights of soil in figure 1 can be calculated.



When carrying out routine tests it is not necessary to measure both green and yellow colors. Only the green color is measured in this laboratory, as the in-

TABLE 1  
*Colors of dichromate solutions*

DICHROMATE TREATED AS SOIL SOLUTION	EXTINCTION VALUES WITH VIOLET FILTERS		
	Extinction measured	Correction	Corrected value
<i>ml.</i>			
10	0.84	Nil	0.84
8	0.65	0.01	0.66
5	0.38	0.03	0.41

TABLE 2  
*Comparison of extinction values obtained with red and violet filters*

SOIL NUMBER AND WEIGHT OF SAMPLE	EXTINCTION	
	Red filter	Violet filter
123, $\frac{1}{2}$ gm.	0.37	0.61
	0.34	0.62
	0.38	0.57
	0.37	0.62
Average.....	0.37	0.61 [0.61]*
123, 1 gm.	0.59	0.38
	0.62	0.40
	0.64	0.38
	0.60	0.42
	0.61	0.45
Average.....	0.61	0.41 [0.40]
256, $\frac{1}{2}$ gm.	0.50	0.54 [0.50]
285, $\frac{1}{2}$ gm.	0.55	0.44
	0.57	0.41
Average.....	0.56	0.43 [0.45]
456, $\frac{1}{2}$ gm.	0.42	0.56 [0.57]
456, 1 gm.	0.72	0.30 [0.28]

\* Bracketed figures represent values that would be obtained from figure 1 as corresponding to the average red values.

strument available is more sensitive with red or orange filters than with violet filters, less manipulation is required, and the dichromate need not be accurately prepared.

If the soil organic matter is not greater than 5.5 per cent, 1 gm. can be taken

for analysis. Usually it is better to take  $\frac{1}{2}$  gm. With the smaller quantity, relative error in a reading is doubled by comparison with 1-gm. tests, but as

TABLE 3

*Results of duplicate analyses by the method described, extinction measured with red filters*

SAMPLE NUMBER	ORGANIC MATTER CONTENT OF SOIL		
	Weight of sample, $\frac{1}{2}$ gm.	Weight of sample, 1 gm.	Over-all average
123	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
	3.0	3.2	
	3.5	3.2	
	3.2	3.7	
	3.5	3.5	
		3.7	
		3.3	
		3.1	
Average .....	3.3	3.4	3.4
256	6.0		
	5.2		
Average .....	5.6		5.6
285	6.2		
	5.8		
	6.2		
	5.4		
Average .....	5.9		5.9
441	2.8	2.5	*
	2.2	2.8	
	3.2		
	2.7		
	3.0		
Average .....	2.8	2.7	2.7
450	2.1	2.4	
	2.7		
Average .....	2.4	2.4	2.4
456	4.2	4.7	
		4.7	
Average .....	4.2	4.7	4.5

\* A test with 0.2 gm. of sample 441 indicated 2.6 per cent.

against this, the absolute error is about halved in reading colors falling on the lower portion of the curve, where the slope is only about half that of the upper

portion. When red or orange filters are used, the increased light transmission at low readings also improves the sensitivity.

To find out whether the shapes of the curves were the same for various soils, a few comparison tests were made with different samples. The results are shown in table 2. Opposite each average value for the violet filter is shown in brackets the value which would be obtained from figure 1 as corresponding to the average red filter value. Agreement is satisfactory.

Table 3 shows results in terms of percentage of organic matter from red filter values. Individual results do not differ by more than 0.5 from the over-all averages. The special soil (containing 3.4 per cent organic matter) used to prepare figure 1 was made by sifting sample 441, which contains 2.7 per cent. Care is obviously necessary that no segregation of different sized particles occurs when the sample is weighed for test, as the finer particles are richer in organic matter.

TABLE 4  
*Comparison of results obtained by original and modified methods*

EXTINCTION, RED FILTER, 4-CM. CELL	ORGANIC MATTER CONTENT OF 1-GM. SOIL SAMPLE	
	Results of modified method	Graham's results
	<i>per cent</i>	<i>per cent</i>
0.12	0.5	0.5
0.26	1.2	1.3
0.41	2.0	2.2
0.60	3.3	3.3
0.70	4.4	4.0

It is interesting to compare the results obtained in this laboratory with those of Graham (2) by converting his transmittancy figure for a 1.5-cm. cell to extinction for a 4-cm. cell. The temperature conditions in this laboratory compare with his No. 2 curve, but as the acid in the method described here was stronger (98.7 per cent), results should be between his No. 1 and No. 2 curves, if the red filters were identical. His filters transmitted an average wavelength of 645 m $\mu$ . Those in this laboratory transmit a band from about 640 to 740 uniformly and a smaller amount down to 580. Results, however, should agree approximately, and actually do, as shown in table 4.

The red filters used in the tests already described were the Spekker No. 1 type from the H.455 set. Subsequently, Spekker Spectrum Red filters No. 608 were tried and found unsuitable, giving a very small "spread" of values. Spectrum Orange filters No. 607 and Orange filters No. 3 from the H.455 set were then tried. These were almost equally good, and both were superior to either of the red filters. The following extinctions were measured on the same soil solution and with different filters:

(a) Spectrum Red No. 608.....	0.57
(b) Red No. 1—H.455.....	0.82
(c) Orange No. 3—H.455.....	1.13
(d) Spectrum Orange No. 607.....	1.29

On plotting (b) readings for several solutions against (d) readings, a straight-line graph was obtained. It was therefore easy to make a new graph correlating (d) readings with organic matter. This will be used in future work for greater accuracy.

#### SUMMARY

By introducing a minor modification (filtration) into Graham's method for determining soil organic matter, work is speeded up and the possibility of error due to turbidity is eliminated. Measurements of the green color of the reduced reagent or of the yellow color of the unreduced give concordant results, indicating that there is no interference from colored matter in incompletely oxidized soil. This is further proof of the soundness of Graham's method. It has been shown how, in laboratories with no facilities for organic combustions, calibration graphs may be prepared by stoichiometrical calculation.

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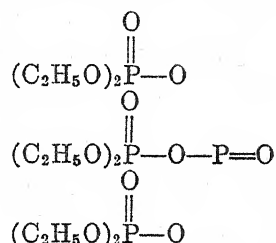
# ANALYTICAL EVALUATION OF CERTAIN SYNTHETIC ORGANIC PHOSPHATES IN RELATION TO THEIR FERTILIZER EFFECTIVENESS IN POT CULTURES<sup>1</sup>

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The insecticide "Bladan" was developed in Germany and was used extensively during the period of World War II (7). It is a viscous hygroscopic product and was thought to be hexaethyl tetraphosphate ( $C_{12}H_{24}P_4$ ) (3). In highly diluted aqueous solution, this organic phosphate was found to be efficacious and was rated superior to nicotine alkaloid in the control of the larvae of red spider mites and of the adults, although it was not lethal to their eggs (5, 9, 10, 18). The compound was designated "H.E.T.P." and was given the structural formula



Hall and Jacobson (6) concluded, however, that "H.E.T.P." is comprised chiefly of tetraethyl pyrophosphate ("T.E.P.P."), with some occurrence of ethyl metaphosphate and triethyl orthophosphate, and with possible incidence of pentaethyl triphosphate. From their recent comparisons of organic phosphates as insecticides, Zimmerman and Hartzell (22) concluded that "T.E.P.P." was decidedly more potent than "H.E.T.P."

Because of earlier reports as to its efficacy in the control of the red spider "H.E.T.P." as suggested for insect control in current greenhouse studies on new types of phosphatic fertilizers at this station. Two questions arose: (a) Would sprays of high dilutions of the organic phosphate impart direct fertilization to the above-ground growth? (b) Would such sprays induce in the soil biochemical effects that might influence the effectiveness of the mineral phosphates that were under evaluation by means of the pot cultures? Consideration of aspect (b) prompted a study of the behavior of "H.E.T.P." as a phosphorus carrier after its direct incorporation. It then became necessary to determine the phosphorus content of that organic in order to compute the quantities to be incorporated in the Neubauer pilot tests and in the pot cultures. Only fractions of the phosphorus of the un-ionized "H.E.T.P." were registered, however, by the procedures

<sup>1</sup> From studies conducted in collaboration with the Tennessee Valley Authority, departments of chemical engineering and agricultural relations.

prescribed for fertilizer analysis (1, p. 127). Analytical recovery was incomplete also when the organic phosphate was subjected to rigorous treatments with perchloric and sulfuric acids, and with prefatory incinerations with magnesium nitrate (8). To bring the phosphorus content of a 10-ml. aliquot of aqueous 0.4 per cent solution of "H.E.T.P." completely into  $\text{PO}_4$ , a prolonged near-boiling digestion in *aqua regia* was found necessary, even though the digestate contained merely 9 to 12 mgm. of phosphorus. Several other true organic phosphates—that is, those devoid of basic elements—then were introduced into the analytical study and, of those, certain ones were found resistant to imposed conditions that were even more rigorous than the conditions of the procedure that was found adequate for analysis of "H.E.T.P." (8).

#### OBJECTIVES

This study was conducted to ascertain whether the fertilizer effectiveness of a synthetic organic phosphate can be foretold by the extent to which generation of  $\text{PO}_4$  is effected through conventional laboratory digestions. Another objective was to learn whether the phosphorus of the organics would be taken up by rye seedlings in pilot Neubauer (21) tests, without conclusion as to the form in which the migration occurs, or even whether the uptaken element would undergo elaboration into plant tissue. It was postulated that plant response to the input of an organic phosphate would indicate whether the chemical and biochemical functions of a properly limested soil could induce conversion of the phosphorus of the organic into meta (11) and ortho forms and assure effective utilization by two successive crops.

#### EXPERIMENTAL

##### *Prefatory analytical evaluations*

The values given in table 1 show that prolonged *aqua regia* digestions of the several organic phosphates failed to register complete transitions to  $\text{PO}_4$ , although the maximal content of phosphorus in any aliquot-digestate was about one eighth of the content prescribed for an analytical charge of a phosphatic fertilizer (1). In three of the analytical charges of the 0.4 per cent solutions of the organics there was no conversion of phosphorus content to ortho form after 4-hour digestions. Moreover, even after 16-hour digestions three of the materials yielded only fractional equivalences of the phosphorus indicated by their formulas, although such digestions did effect complete ortho-transitions of the two phosphates—hexaethyl tetra and monoethyl acid. Initially, five of the six diluted solutions of the organics were devoid of  $\text{PO}_4$ , and only one seventh of the phosphorus content of the monoethyl compound was in ortho form. After a 4-gm.-per-liter solution of "H.E.T.P." had been allowed to stand 6 months at room temperature, however, the phosphorus content had undergone hydrolysis of 40 per cent. Hall and Jacobson (6) cited a German report that in aqueous solution at room temperature "H.E.T.P." was "hydrolyzed completely to ethyl alcohol and orthophosphoric acid," whereas they found no development of ethanol and virtually no generation of  $\text{PO}_4$  in a 10-gm.-per-40-ml. solution after 4 days

at 25°C., although they reported that tetraethyl pyrophosphate "hydrolyzed spontaneously in water to diethyl orthophosphoric acid." In their study of "H.E.T.P." and "T.E.P.P." Hall and Jacobson (6) used "a colorimetric method especially adapted to those products" and its publication was promised.

The partial values obtained by the *aqua regia* digestions of four of the six organics in table 1 are reported to show the inadequacy of the detailed digestions for the analysis of synthetic organic phosphates, whereas specifically determined percentages of phosphorus content (through digestions up to 36 hours) were used to compute the quantities of the organics that were incorporated into the soil in the subsequent Neubauer tests and in the following pot cultures.

TABLE 1

*Effect of the duration of aqua regia digestion\* of aliquots of certain organic phosphates upon the ionization of their phosphorus content*

PHOSPHATE			P <sub>2</sub> O <sub>5</sub> FOUND AFTER DIGESTIONS FOR VARIOUS PERIODS			
Type	Formula	Theoretical P <sub>2</sub> O <sub>5</sub> content	4 hours	5 hours	7 hours	16 hours
		per cent	per cent	per cent	per cent	per cent
Hexaethyltetra.....	C <sub>12</sub> H <sub>30</sub> O <sub>13</sub> P <sub>4</sub>	56.0	22.2†	30.6	44.6	55.3
Hexaethyltetra‡§.....	C <sub>12</sub> H <sub>30</sub> O <sub>13</sub> P <sub>4</sub>	28.0	0.0	....	....	23.7
Triethyl.....	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> O <sub>3</sub> PO	38.6	3.2	9.4	....	....
Tricresyl§.....	(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>3</sub> O <sub>3</sub> PO	19.2	0.0	0.0	....	3.0
Triphenyl§.....	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> O <sub>3</sub> PO	21.8	0.0	0.0	....	11.9
Monoethyl¶.....	C <sub>2</sub> H <sub>5</sub> H <sub>2</sub> PO <sub>4</sub>	56.3	36.0	....	....	57.2

\* Made at 120°C. upon 10-ml. aliquots of 250-ml. solutions of a 1-gm. charge.

‡ A commercial product, "Vapotone," labelled as containing "50% active ingredients."

§ Alcoholic solution.

¶ An undigested aliquot gave 8.75 per cent P<sub>2</sub>O<sub>5</sub> through direct molybdate precipitation, as indicative of 15 per cent ionization.

† Contents of 7.3 per cent and 11.4 per cent of P<sub>2</sub>O<sub>5</sub> were registered after 1 hour and after 2 hours, respectively.

#### *Pilot Neubauer tests*

Readiness of uptake of phosphorus from the organics was measured by the Neubauer procedure, through the technique prescribed by Thornton (21). Each culture of Clarksville silt loam received an input equivalent to 25 mgm. of P<sub>2</sub>O<sub>5</sub>, and the growth period was 17 days.

#### *Soil and incorporations*

Clarksville silt loam of the pot cultures was known to be responsive to phosphates and hence was used in the Neubauer tests. It was processed in bulk through, incorporations of 100-mesh high-calcic limestone at the rate of 2 tons per 2,000,000 pounds of soil, and the bulk then was divided quantitatively for the mixing in of the respective phosphates.

Concentrated superphosphate and two forms of dicalcium phosphate served as

controls at rates of 80 and 320 pounds of  $P_2O_5$  per-acre-surface and were incorporated into the upper half of the potted soil along with 185-pound additions of  $K_2SO_4$ .

Five of the organics were liquid, but the tricresyl and triphenyl phosphates and the non-aqueous solution, "Vapotone," were not miscible with water. The triphenyl phosphate was a flaky solid. Hence, to assure uniformity of incorporation, aliquots of the immiscible phosphates were dissolved in alcohol and the resultant alcoholic solutions were introduced into the soil in parallel with the aqueous solutions of the other three organics of table 1, by means of the following procedure: The analytically determined charge of each phosphate solution was introduced into 200 gm. of 20-mesh dry quartz. The phosphate-quartz mixture was allowed to dry and then was mixed into 400 gm. of the upper half of the potted soil. The resultant 600-gm. mixture of the organic phosphate-impregnated quartz and soil then was incorporated into the full upper half of the soil in the pot. Each solid phosphate control was incorporated in that form in like manner. Otherwise, the technique used in the greenhouse studies was the one previously described (12).

#### NEUBAUER AND POT CULTURE RESULTS

In the prefatory Neubauer tests by means of rye seedlings, highest uptake of phosphorus from the limestoned Clarksville silt loam was from the hexaethyl tetraphosphate, as such and as "Vapotone," and was somewhat more than the uptake from the monocalcium phosphate control. The uptake from the monoethyl acid phosphate was intermediate and greater than that from the two types of dicalcium phosphate. The monoethyl acid orthophosphate showed the most ready hydrolysis in the digestions recorded in table 1. Uptake from the triphenyl compound was meager, whereas there was none from the triethyl phosphate, the 5-hour analytical hydrolysis of which was 24 per cent in contrast to nil for the tricresyl and triphenyl phosphates.

Successive crops of Sudan grass and ryegrass were used to ascertain fertilizer effectiveness of the un-ionized organics and phosphorus recoveries therefrom through comparisons with monocalcium and dicalcium phosphates (table 2, fig. 1). These comparisons involve the effectiveness of phosphorus in a form not conducive to fixation and the effectiveness of that element when it is incorporated in the two ortho forms, one of which undergoes fixation speedily.

Measured by the over-all responses to the input of phosphorus at the two rates and by its uptake in the pot cultures, virtually the same effectiveness was registered by Wilson Dam superphosphate, hexaethyl tetraphosphate, diluted hexaethyl tetraphosphate ("Vapotone"), and monoethyl acid orthophosphate. Although the two forms of dicalcium phosphate (anhydride and stabilized dihydrate) proved somewhat more effective than the other phosphates for the 80-pound input of  $P_2O_5$ , these secondary phosphates did not show like superiority at the 320-pound rate. This relationship is in harmony with the probability of response to heavy-rate incorporations of secondary and tertiary calcium phosphates on limestoned soil.

TABLE 2

Fertilizer effectiveness of the phosphorus of certain difficultly ionizable organic phosphates on Clarksville silt loam\* as registered through phosphorus uptake and crop growth

PHOSPHATES USED			POT NUM- BER	"GRASS" CROP	P <sub>2</sub> O <sub>5</sub> INCORPORATIONS† PER ACRE SURFACE						NEUBAUER UPTAKE OF P <sub>2</sub> O <sub>5</sub> ‡	
Type	Formula	P <sub>2</sub> O <sub>5</sub> con- tent			80 pounds			320 pounds				
					Dry weight	P <sub>2</sub> O <sub>5</sub>		Dry weight	P <sub>2</sub> O <sub>5</sub>			
		per cent			gm.	per cent	mgm.	gm.	per cent	mgm.	mgm.	per cent§
None	....	....	12S	Sudan	2.8	0.32	9	....	....	....	....	....
				Rye	1.8	0.34	6	....	....	....	....	
				Total	4.6		15					
Wilson Dam super		50.5	132	Sudan	13.8	0.46	63	22.2	0.57	127	14.4	58%
				Rye	9.0	0.39	35	14.9	0.81	121		
				Total	22.8		98	37.1		248		
Dicalcium (an- hydrous)	CaHPO <sub>4</sub>	50.8	154	Sudan	16.7	0.47	78	18.9	0.57	108	6.5	26
				Rye	10.1	0.40	40	15.5	0.82	127		
				Total	26.8		118	34.4		235		
Dicalcium (di- hydrate sta- bilized)	CaHPO <sub>4</sub> ·2H <sub>2</sub> O	40.9	156	Sudan	16.7	0.48	80	18.8	0.60	128	7.1	28
				Rye	9.8	0.39	38	13.4	0.80	107		
				Total	26.5		118	32.2		235		
Hexaethyl tetra	C <sub>12</sub> H <sub>30</sub> O <sub>13</sub> P <sub>4</sub>	55.3	136	Sudan	12.5	0.40	61	20.7	0.60	124	15.5	62
				Rye	8.9	0.44	39	14.9	0.72	107		
				Total	21.4		100	35.6		231		
Hexaethyl tetra	C <sub>12</sub> H <sub>30</sub> O <sub>13</sub> P <sub>4</sub>	28.7	138	Sudan	12.7	0.46	58	21.9	0.60	131	16.5	66
				Rye	7.6	0.44	33	14.7	0.71	104		
				Total	20.3		91	36.6		235		
Triethyl	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> O <sub>3</sub> PO	37.4	186	Sudan	1.8	0.34	6	2.1	0.31	7	0	0
				Rye	1.8	0.34	6	1.3	0.33	4		
				Total	3.6		12	3.4		11		
Tricresyl	(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>3</sub> O <sub>3</sub> PO	17.0	140	Sudan	7.0	0.60	42	6.0	0.69	41	4.1	16
				Rye	12.0	0.39	47	20.9	0.81	169		
				Total	19.0		89	26.9		210		
Triphenyl	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> O <sub>3</sub> PO	18.1	142	Sudan	10.9	0.66	72	13.8	0.72	99	1.6	6
				Rye	9.6	0.44	42	15.9	0.93	148		
				Total	20.5		114	29.7		247		
Monoethyl acid orthophos- phate	C <sub>2</sub> H <sub>5</sub> H <sub>2</sub> PO <sub>4</sub>	57.5	144	Sudan	13.5	0.49	66	20.5	0.59	121	8.5	34
				Rye	8.4	0.41	34	13.5	0.73	99		
				Total	21.9		100	34.0		220		

\* Initial pH 5.4, before full-depth 2-ton incorporation of 100-mesh limestone.

† Basis of total content.

‡ By rye seedlings from 25 mgm. of P<sub>2</sub>O<sub>5</sub> per culture.

§ In relation to the 25-mgm. input.

¶ Monocalcium phosphate was used in this culture.

|| "Vapotone"—a commercial product.



The effectiveness of the two hexaethyl tetraphosphate products indicated that the dilution that prevailed in the soil system was such as to induce rapid hydrolysis in keeping with that attributed by Hall and Jacobson (6) to very

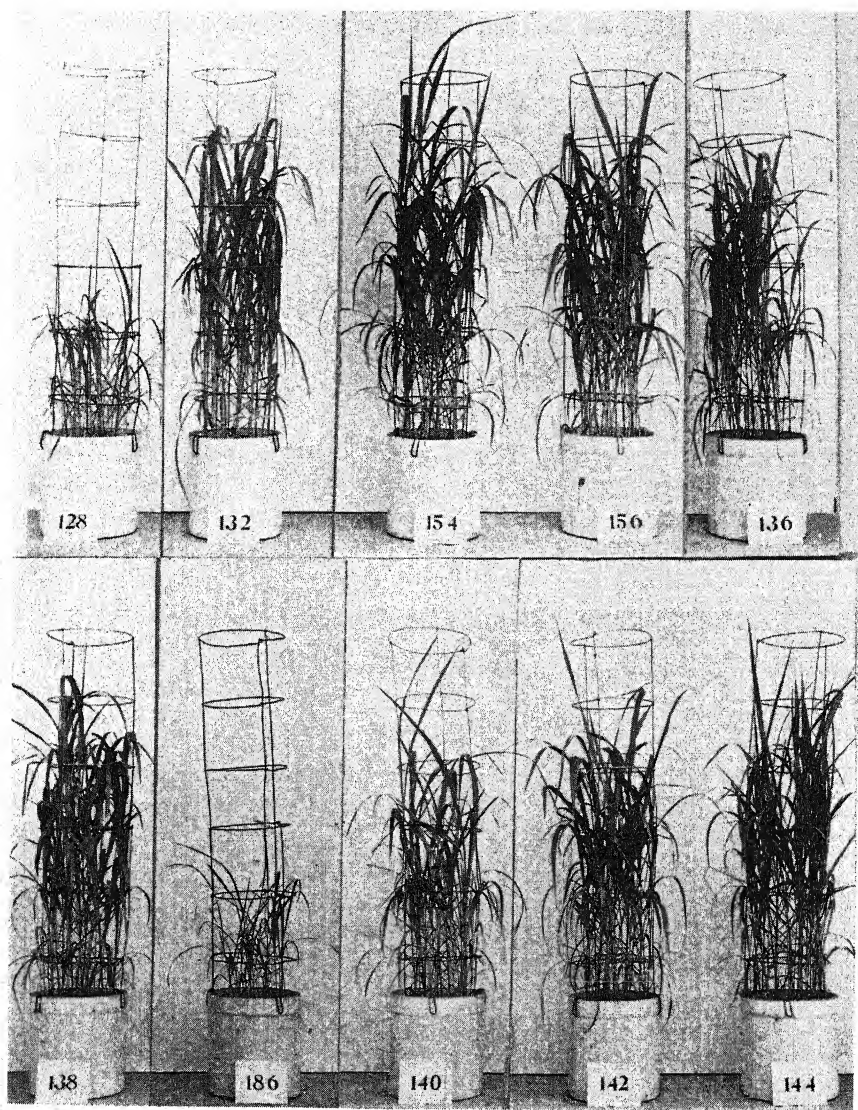


FIG. 1. RESPONSE BY SUDAN GRASS TO THE ORGANIC PHOSPHATE LISTED IN TABLE 2  
Input rate of 80 pounds of  $P_2O_5$  equivalence

dilute solutions and with resultant plant utilization equal to that from the  $PO_4$  of the superphosphate.

Since there was no uptake of the phosphorus from the triethyl phosphate by either the rye seedlings in the Neubauer tests or the crops of Sudan grass and

ryegrass, there was no increase in the growth of either of those crops. Hence appreciable conversion of its content of phosphorus to  $\text{PO}_4$  in the soil is deemed improbable, especially since only one twelfth of the small charge of phosphorus in its analytical aliquot was converted to ortho state during 4 hours' near-boiling digestion (table 1). It therefore appears that during its continuation as such in the soil system the triethyl phosphate exerted a toxic effect that extended through the growth of the second crop. This postulation is deemed probable, although the 5-hour digestion of triethyl phosphate induced a 24 per cent hydrolysis in contrast to nil for the tricresyl and triphenyl phosphates, both of which induced substantial response in growth and in the phosphorus content of the ryegrass which followed Sudan grass.

Even though the digestates of their analytical aliquots did not contain determinable incidence of  $\text{PO}_4$  after a 5-hour digestion, the tricresyl and triphenyl phosphates did register some Neubauer uptake and both induced an increase in the growth of ryegrass. Although the responses by Sudan grass to tricresyl phosphate, at the 80-pound and 320-pound rates for  $\text{P}_2\text{O}_5$  input, were about half of the corresponding responses shown to Wilson Dam superphosphate, the tricresyl phosphate induced the highest responses of ryegrass to the 80-pound and the 320-pound incorporations of  $\text{P}_2\text{O}_5$  and also induced phosphorus compositions identical with those found for the superphosphate. Hence, the largest uptake of phosphorus by the rye crop was that from the tricresyl phosphate, although only one sixth of the phosphorus content of its analytical aliquot had been converted to  $\text{PO}_4$  during 16 hours of analytical digestion. It may be that the soil effected a transition of the P content of the tricresyl phosphate to  $\text{PO}_4$  in time for the assimilation of that radical by the ryegrass, or that crop may possess a specific ability to take up and utilize the organic phosphate as such or as its meta derivative (11).

#### DISCUSSION AND SUMMARY

The extent to which the phosphorus content of a small aliquot of a true, or base-free, organic phosphate undergoes analytical conversion to  $\text{PO}_4$  does not serve as an infallible forecast for either the extent of phosphorus uptake by rye seedlings or the effect of the organic upon the growth and phosphorus content of certain plants.

In concentrated form "H.E.T.P." and "T.E.P.P." are devoid of  $\text{PO}_4$  and are decidedly stable, whereas these two organics undergo hydrolytic change rapidly in high dilution. When they undergo conversion to  $\text{H}_3\text{PO}_4$ , however, both materials lose their insecticidal values and acquire fertilizer effectiveness. The monoethyl acid orthophosphate was alone in showing incidence of  $\text{PO}_4$  initially, yet only 64 per cent of the phosphorus content of its highly diluted aliquot was in the ortho state after the 4-hour near-boiling digestion. In the present study the organics were incorporated into the soil before seeding and no attempt was made to ascertain whether the highly diluted solutions would have influenced plant response had the solutions been sprayed upon the above-ground growth. Since extremely high dilutions of these materials are prescribed for insecticidal

control, the quantity of phosphorus absorbed by the sprayed plant tissue would be meager and probably would not influence the responses to the incorporated experimental phosphatic fertilizers.

The relative values of natural occurrences of organic and inorganic forms of phosphorus in soils and the fertilizer value and mineralization behavior of certain synthetic organic phosphates have been dealt with (4, 13, 15, 16, 17, 19), and the over-all subject of phosphorus in soils and plants was elaborated by Pierre (14). Certain organic phosphates have been proposed as media to induce the migration of additive phosphorus in soils and to delay the rapid fixation that ensues when that element is incorporated in the meta and ortho forms (2, 20). The phosphates of the present paper are of more recent development, however, and are true organics and devoid of any basic element. Moreover, the objectives of the present study were different in that the intent was to integrate the acidic digestion values for the several organic phosphates with the phosphorus uptake by rye seedlings, and with crop response and phosphorus content.

Although the analysis of industrial phosphatic materials by the conventional analytical procedures is used as a measure of their fertilizer value, the behavior of a synthetic organic phosphate in the soil and its effect upon plant growth cannot be foretold by those procedures. The possible nutritional benefit to plant growth through an uptake of phosphorus from the sprayed organic is offset by certain observations as to detrimental effects of the sprays upon the upper foliage (22). That aspect was recognized but was not dealt with in the present study.

The findings obtained in the tests of the six organics of tables 1 and 2 warrant the stipulation that the phosphorus content of a synthetic organic phosphate should be determined by means of a technique specifically adequate, whereas its efficacy as a source of nutrient phosphorus should be determined through integrated pot cultures.

Even though every included organic phosphate, other than the tricresyl compound, induced an uptake of phosphorus and caused a substantial increase in over-all plant growth, the synthetic organic phosphates could not compete with inorganic phosphatic fertilizers, and their inclusion in fertilizer experimentation probably will extend solely to their intended use for insecticidal control. When an organic phosphate is to be included in experimental fertilizer comparisons, its phosphorus content, its form, and its resistance to hydrolysis should be determined by means of a specifically proved analytical procedure.

Whatever may be the use to which the synthetic organic phosphates are to be put, it is imperative that an analytical procedure be evolved for the rapid and accurate determination of their phosphorus contents. Of the methods now official for the determination of the phosphorus content of fertilizers (1), none serves to register the full phosphorus content of the synthetic organic phosphates.

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# SOME EFFECTS OF FLUORINE ON PEACH, TOMATO, AND BUCKWHEAT WHEN ABSORBED THROUGH THE ROOTS<sup>1</sup>

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Accompanying the rapid progress in chemistry during the war years have been certain disadvantages arising from injury to plant and animal life caused by release into the air of noxious gases from industrial plants. Among the suspected gases is fluorine, to which considerable damage to crops and farm animals has been attributed by farmers in widely scattered industrial areas throughout the country (1, 3, 4).

With the hope of gaining some insight into the problem, this preliminary experiment concerning the effects of fluorine absorption by plants was undertaken. These data will serve as a basis for more thorough investigation into the relationship between fluorine and plant life.

The specific objectives of this experiment were to ascertain: (1) amounts of fluorine required in the substrate to produce visible injury in the plant when sodium fluoride is absorbed through the roots; (b) the length of time required for the plant to show external symptoms of fluorine injury; (c) the characteristic pattern of injury produced on plant foliage as a result of fluorine absorption through the roots; (d) the relation between the amount of fluorine in the substrate and that accumulated in the plant tissue.

## PLAN OF EXPERIMENT

Three unrelated plant species; namely peach, tomato, and buckwheat, were selected for the experiment.

Seedlings of each of these species were transplanted to acid- and alkali-washed white quartz sand in glazed porcelain pots treated with a complete standard nutrient solution containing the major salts in the following molar concentrations: 0.001 M  $\text{Ca}(\text{NO}_3)_2$ , 0.004 M  $\text{KNO}_3$ , 0.0010 M  $\text{MgSO}_4$ , 0.0010 M  $\text{KH}_2\text{PO}_4$ , and 0.0005 M  $(\text{NH}_4)_2\text{SO}_4$ , as well as trace amounts of the minor elements, B, Mn, Zn, and Fe. The continuous drip culture method of Shive and Stahl (5) was used. When the plants were ready for fluorine treatment, the pots were fitted with paraffin-coated cardboard covers containing an opening through which a glass tube from the culture vessel carried the fluorine-containing nutrient solution into the sand without exposure to the air. The waste solution was carried away through a closed drainage system to minimize effects of the escape of fluorine into the air. Fluorine in the form of sodium fluoride was incorporated into the nutrient solution to produce the following concentrations: 0, 1, 5, 10,

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, departments of plant physiology and plant pathology.

25, 100, 200, and 400 p.p.m. of fluorine. Two liters of nutrient solution were applied daily. Observations were made daily. At harvest, green and dry weights were determined. Aliquots of these plant tissues were prepared for fluorine analysis by drying for 48 hours at 45°C. and grinding through a 60-mesh screen of a semimicro Wiley mill. The fluorine content of plant tissues was determined by a method used by Glen Edgington of the U. S. Department of Agriculture. In brief, the analytical procedure was as follows:

A 3-gm. sample of plant tissue mixed with 1 gm. of CaO and moistened with distilled water was ignited in a platinum dish in a muffle at 600°C. Distillation was by the Willard-Winter method (6). The ash residue was transferred to a distilling flask, and 35 ml. of 70 per cent perchloric acid was added. With the temperature in the distilling flask at 135°C., two 250-ml. fractions of distillate were collected in a flask containing 15 ml. of H<sub>2</sub>O and 2 ml. of 0.05 N NaOH

TABLE 1  
*Results obtained from fluorine absorption through the roots of peach seedlings*

F IN NUTRIENT SOLUTION	INTERVAL BEFORE INJURY APPEARED	DATE OF HARVEST	CONDITION AT HARVEST		FLUORINE CONTENT	
			Leaves	Roots	Leaves	Stems
<i>p.p.m.</i>	<i>days</i>				<i>p.p.m.</i>	<i>p.p.m.</i>
400	1	August 8	Plant killed	Dead	1442	1286
200	2	August 8	Plant killed	Dead	455	367
100	3	August 17	Plant killed	Dead	550	144
50	10	August 21	Tips and margins of leaves injured	Dead	232	48
25	10	August 21	Tips and margins of leaves injured	Majority dead	261	52
10	10	August 21	Tips and margins of leaves injured	Majority dead	220	5
0	No injury	August 21	No injury	No injury	6	0

solution, at the rate of 50 ml. per 20 minutes. Aliquots of these fractions were used to determine the fluorine content.

The titration was carried out according to the back titration of Dahle, Bonnar and Wiehman (2). Twenty-five milliliters of the distillate was pipetted into a Nessler tube, and a blank containing 25 ml. of distilled water was prepared. To each tube was added 1 ml. of hydroxylamine hydrochloride, 1 ml. of alizarin red indicator, sufficient 0.05 N NaOH to neutralize, and finally 2 ml. of 0.05 N HCl. Thorium nitrate solution was added to the sample tube until the color changed to a faint pink. Exactly the same amount of thorium nitrate was added to the blank. Standard sodium fluoride solution was added to the blank until the colors of the two tubes matched. The fluorine content of the sample tube was equal to the amount of fluorine added to the blank tube. Blanks were run with perchloric acid and CaO and the correction was applied to the results.

#### PEACH

Nine peach seedlings about 6 inches tall, of uniform appearance but undetermined inheritance, were selected. They were transplanted, as previously de-

scribed, on May 21, 1946. Complete standard nutrient solution was applied daily until July 30, when the fluorine treatments were begun.

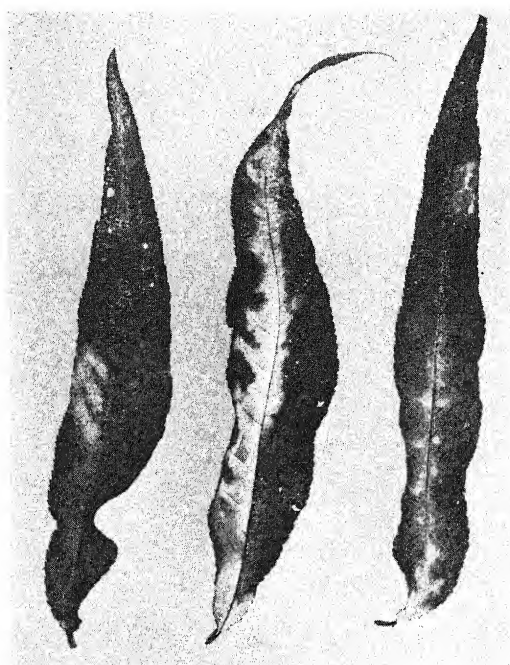


FIG. 1. EFFECT OF 400 P.P.M. FLUORINE IN SUBSTRATE ON PEACH LEAVES 1 DAY AFTER START OF TREATMENT

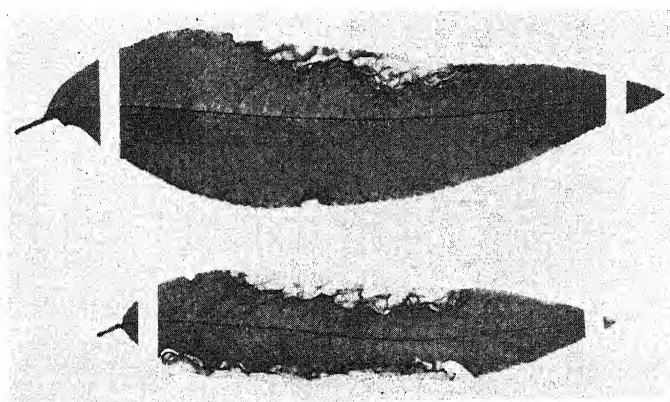


FIG. 2. MARGINAL BURNING OF PEACH LEAVES CAUSED BY 25 P.P.M. FLUORINE IN SUBSTRATE 3 WEEKS AFTER START OF TREATMENT

As shown in table 1, the time required for appearance of symptoms of fluorine injury decreased, in general, as the fluorine concentration in the substrate increased. At the higher concentrations, 200 and 400 p.p.m. fluorine, peach seedlings manifested similar stages in the development of fluorine-toxicity symp-

toms. First the plants became severely wilted. Scorching then occurred, extending out from the petiole along the veins, evidently following the translocation stream. Gradually the scorching enveloped all the leaf and stem tissue. Within 4 days after the start of fluorine treatment, both plants were dead. The scorched areas which were brown in the beginning were bleached to a buff color within a short time.

At concentrations of 10 to 100 p.p.m. fluorine, the pattern of injury produced on peach seedlings was unlike that observed at the higher concentrations. The first sign of fluorine injury on these plants was a scorching of the tips of the younger leaves. This scorching continued from the tips along the margins of the younger leaves and occasionally into the leaf blades. The older leaves very often showed marginal burning without first having shown tip injury. Injury to the plants treated with 10 and 25 p.p.m. fluorine proceeded no further, but on the plant treated with 100 p.p.m. fluorine the scorching spread over all the leaves until the plant was killed. Common to all plants treated with fluorine was the characteristic browning of the roots.

Analyses showed that, in general, as the amount of fluorine in the substrate was increased, the total fluorine content in the plant tissues increased. The leaves had a much greater fluorine content than the stems. Minor variations from this general trend might be attributed to differences in genetic constitution of the individual peach seedlings.

#### TOMATO

Twenty-seven uniform Rutgers tomato seedlings were transplanted on September 15, 1946 and given a complete standard nutrient solution. On October 8, fluorine treatment was started. All plants were harvested December 13, 1946. The data have been compiled in table 2.

As with peaches, the time required for appearance of injury symptoms due to fluorine decreased progressively as the amount of fluorine in the substrate was increased. As a result of the highest concentrations of fluorine, the tomato leaves became wilted. The younger leaves appeared water-soaked and the stems were darkened. Scorching set in along the previously discolored areas extending from the petiole into the leaf. The affected regions were bleached to a characteristic buff color. By the end of the experiment these plants were dead. Concentrations from 25 to 100 p.p.m. fluorine produced a similar pattern of injury on tomato leaves, in that injury started at the tips of the younger leaves and later appeared along the margins. At 100 p.p.m., injury was not confined to the margin but spread inward on the leaf blade. Below 10 p.p.m. fluorine no injury was produced. The appearance of the roots reflected the condition of the tops of the plants. At the higher concentrations of fluorine in the substrate, growth was retarded and the root systems were discolored. The plants in this series were allowed to set fruit, on which observations were made. The plants treated with 200 and 400 p.p.m. fluorine died before fruit set. Concentrations of 10, 25, 50, and 100 p.p.m. fluorine appeared to induce blossom-end rot. An interesting fact is that this condition of the fruit appeared at 10 p.p.m. fluorine

where there were no other symptoms of fluorine injury on leaves or roots. Plants given 0, 1, and 5 p.p.m. fluorine in the substrate produced normal fruit.

TABLE 2

*Results obtained from fluorine absorption through the roots of Rutgers tomatoes*

F IN NUTRIENT SOLUTION	INTERVAL BEFORE INJURY APPEARED	CONDITION AT HARVEST			FLUORINE CON- TENT	
		Leaves	Roots	Fruits	Leaves	Stems
<i>p.p.m.</i>	<i>days</i>				<i>p.p.m.</i>	<i>p.p.m.</i>
400	2	Dead	Dead—very small	No fruit set	2179	
200	5	Dead	Small—brown	No fruit set	1824	127
100	18	Moderate scorching	Small—brown	Blossom end- rot	499	28
50	27	Slight marginal scorching	Small—brown	Blossom end- rot	379	13
25	48	Slight marginal scorching	Normal size- brown	Blossom end- rot	277	9
10	No injury	No injury	No injury	Blossom end- rot	82	15
5	No injury	No injury	No injury	No injury	26	14
1	No injury	No injury	No injury	No injury	14	12
0	No injury	No injury	No injury	No injury	10	12



FIG. 3. EFFECT ON TOMATO LEAVES OF 25 P.P.M. FLUORINE IN SUBSTRATE

Analyses showed that as the fluorine concentration increased in the substrate, fluorine absorption by the plant increased. The amount of fluorine in the leaves greatly exceeded that in the stems.



TABLE 3

*Results obtained from fluorine absorption through the roots of buckwheat*

F IN NUTRIENT SOLUTION	INTERVAL BEFORE INJURY APPEARED	DATE OF HARVEST	CONDITION AT HARVEST		P.P.M. FLUORINE CONTENT OF COM- POSITE SAMPLE
			Leaves	Roots	
<i>p.p.m.</i>	<i>days</i>				<i>p.p.m.</i>
400	2	August 16	Dead	Dead	1910
200	2	August 26	Dead	Dead	716
100	3	August 26	Majority dead	Dead	506
50	4	August 26	Margins of many leaves injured	Moderate injury	580
25	13	August 26	Some injured	Moderate injury	533
10	No injury	August 26	No injury	No injury	101
5	No injury	August 26	No injury	No injury	62
1	No injury	August 26	No injury	No injury	36
0	No injury	August 26	No injury	No injury	16

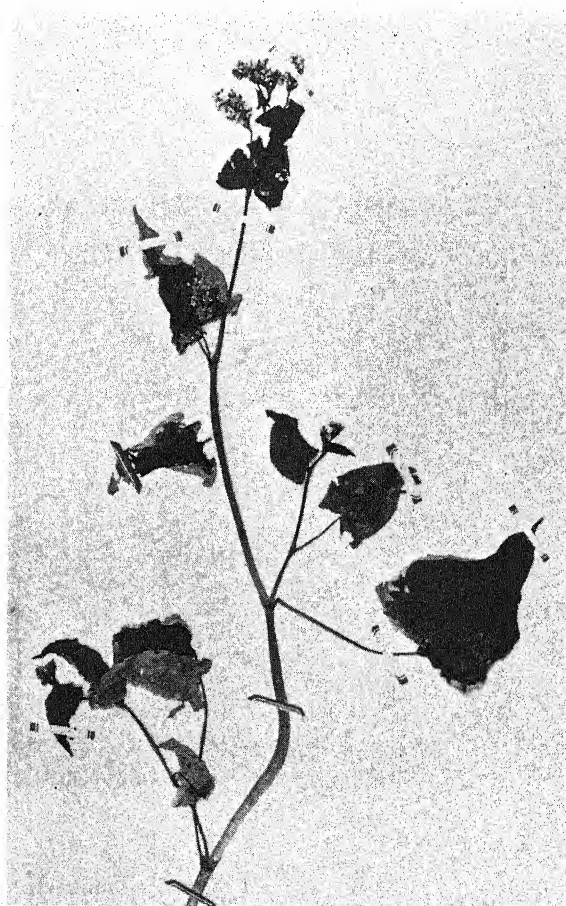


FIG. 4. INJURY TO BUCKWHEAT LEAVES CAUSED BY 200 P.P.M. FLUORINE IN SUBSTRATE

## BUCKWHEAT

Japanese buckwheat seeds were sown directly in experimental pots on July 25, 1946, and fluorine treatments were started on August 13. The results of this experiment are recorded in table 3.

As in peach and tomato, fluorine accumulation in buckwheat varied generally as the concentration of fluorine in the substrate. The time required to show injury again depended on the amount of fluorine in the substrate: plants receiving the most fluorine showed injury soonest. At concentrations of 200 and 400 p.p.m. fluorine in the substrate, buckwheat leaves soon became extremely wilted. The margins of the leaves then had a gray or ashen appearance. These areas soon became scorched and were bleached to a buff color. Injury continued to spread over the entire plant. The plants died within 3 days after treatment with 400 p.p.m. fluorine was begun and within 7 days after treatment with 200 p.p.m. A concentration of 100 p.p.m. fluorine produced a similar pattern of injury, but it did not proceed so far as to bring about death of the plant by the end of the experiment. Concentrations of 1, 5, and 10 p.p.m. fluorine did not cause any visible injury to the buckwheat plants. In this case it was necessary to use a composite sample of stem and leaf tissue for analysis.

## SUMMARY AND CONCLUSIONS

Concentrations of 200 and 400 p.p.m. of fluorine in the nutrient solution caused the death of peach, tomato, and buckwheat plants in a short time.

At a concentration of 100 p.p.m. fluorine, peach and buckwheat were severely injured in 3 days, whereas tomato required a considerably longer time, 18 days, for symptoms to appear.

At concentrations of 10, 25, and 50 p.p.m. fluorine, peach and buckwheat were moderately injured within 13 days, whereas tomato required as long as 48 days for symptoms to appear.<sup>2</sup>

At a concentration of 10 p.p.m. fluorine, peach leaves showed injury, but neither tomato nor buckwheat showed any foliage damage.

At concentrations below 10 p.p.m. fluorine in the nutrient solution, no injury appeared in any of the species under the conditions of these experiments.

The general pattern of foliage injury in the plants treated with medium concentrations of fluorine appeared to be similar for all three species. Where actively growing plants were involved, injury first appeared on the tips of the younger leaves then extended along the leaf margin and finally inward toward the midrib. In each case the injury appeared as a scorching of the affected areas; however, when injury symptoms appeared on peaches approaching the dormant stage the youngest fully expanded leaves first showed injury in the form of marginal scorching. At the highest fluorine concentrations, necrosis was preceded by a general wilting of the plant, probably as a result of root injury. The injury in this case progressed from the petioles and veins outward through the

<sup>2</sup> Subsequent experimentation has shown that though the order in which increasing fluorine concentrations produce injury in the plant remains the same, the length of time required varies with the growth status of the plant and environmental conditions.

leaf blades. Here again there was a bleaching of the original brown color to a buff color with time.

In all three plant species, fluorine accumulation in the tissues varied with the amount of fluorine in the nutrient substrate, increasing as the fluorine concentration was increased.

In every case the amount of fluorine in the leaves greatly exceeded that of the stems.

Because of the preliminary nature of these experiments, no attempts have been made to predict specifically the fluorine accumulation necessary to produce typical foliage injury, especially since more recent work seems to indicate that this accumulation may vary with plant species, growth status, light, and moisture relationships.

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# EFFECT OF TEMPERATURE OF INCUBATION OF AMENDED SOIL ON EXCHANGEABLE MANGANESE<sup>1</sup>

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Manganese is present in soil as the bivalent ion and the insoluble higher oxides. The bivalent ion may be present in the soil solution, held on the exchange complex, or in a nonexchangeable form (6). The bivalent manganese may be oxidized to the insoluble higher oxides by soil microorganisms at near neutral pH values (5), and the higher oxides may be reduced by organic matter or by biological processes (6). Waterlogging at a high temperature also liberates large amounts of soluble manganese (8). The rate of release of insoluble manganese to a soluble form is increased with increasing incubation temperature (2).

The water-soluble and exchangeable bivalent manganese ions, and the higher oxides that can be readily reduced by 0.2 per cent quinol, are considered available to plants (9). The following investigation is concerned with the effects of the decomposition of crop residues by soil microorganisms on the availability of soil manganese as determined by ammonium acetate extraction.

## EXPERIMENTAL

Chopped oat straw and alfalfa meal at a carbon-nitrogen ratio of 30:1 and a nitrogen level of 200 pounds per acre were incorporated in Merrimac sandy loam at 20 per cent moisture and incubated in quart jars with screw caps permitting gas exchange as described in an earlier paper (4). At the indicated intervals, the soil was thoroughly mixed by rotating the jar, and 20.0-gm. samples were removed. The soil sample was shaken for 30 minutes with 210 ml. extracting solution (redistilled water; neutral, normal ammonium acetate; or ammonium acetate containing 0.2 per cent quinol) and then filtered under suction. This procedure follows that described by Sherman *et al.* (9) except that separate samples were taken for each extracting solution.

Two hundred milliliters of the filtrate was evaporated to dryness and digested with 10 ml. of a 1:1 mixture of nitric and perchloric acids after predigestion with 5 ml. of nitric acid. The organic-matter-free salts were evaporated to dryness with 5 ml. of 1:1 HCl to convert difficultly soluble oxides, and the salts were then dissolved in hot, dilute nitric acid. Manganese determinations were made according to Peech's periodate method (7), the color intensities being determined with a Fisher electrophotometer, using 12-mm. absorption cells and a combination filter (Corning 4303 and 3486) with a maximum transmission at 525 m $\mu$ .

Percentage moisture was determined each day on the soil incubated at 47°C.,

<sup>1</sup> Contribution No. 675 from Massachusetts Agricultural Experiment Station, department of bacteriology and public health, Amherst.

and water was added by pipette to replace that lost by evaporation. At lower temperatures only infrequent checks were necessary.

Duplicate jars were carried throughout the experiments, single samples being taken from each jar at each sampling period. All reagents, where possible, were purified by redistillation from pyrex. Blanks on the reagents were not large enough to necessitate correction.

#### RESULTS

A preliminary experiment at 37°C. (table 1) showed that only the exchangeable manganese was affected by incubation. Water-soluble and easily reducible manganese showed no significant variations. Consequently, in all following work, only the exchangeable manganese was studied.

TABLE 1

*Effect of decomposition of organic matter (oat straw and alfalfa meal) on water-soluble, exchangeable, and easily reducible manganese in Merrimac sandy loam at 37°C.*

INCUBATION	MICROGRAMS MANGANESE PER 10.0 GM. DRY SOIL					
	Water-soluble		Exchangeable		Easily reducible	
	Unamended	Amended*	Unamended	Amended*	Unamended	Amended*
<i>days</i>						
0	0.4	0.9 ± 0.2	1.3	7.1 ± 0.7	226	200 ± 4
1	0.4	0.7 ± 0.1	1.6	22.8 ± 3.0	216	199 ± 2
2	0.7	1.1 ± 0.5	1.9	23.5 ± 2.3	233	189 ± 1
3	0.3	1.2 ± 0.5	1.7	23.0 ± 0.1	217	192 ± 6
4	0.5	0.7 ± 0.3	1.7	18.2 ± 2.0	221	199 ± 3
7	0.4	0.5 ± 0	1.6	11.7 ± 3.4	222	180 ± 3
14	0.3	0.4 ± 0.1	0.7	4.9 ± 0.9	187.5	170 ± 5

\* Average value and mean variation of duplicate samples.

Incubations were carried out at 4°, 14°, 30°, 37°, and 47°C. The results of the temperature studies are shown in table 2. From 4° to 30°C., there was only a slight rise in exchangeable manganese, the peak being reached on the third day, followed by a decrease to the initial level after 1 to 2 weeks. From 37° to 47°C., there was a much greater rate of increase of exchangeable manganese and the increase tended to be maintained over a longer period. If the increases in manganese at the third day (peak values) are plotted against temperature of incubation on semilog paper, it is seen that the rate of increase for the first 3 days as a function of temperature above 30°C. is logarithmic (fig. 1).

Of interest also are the data showing that at all temperatures up to and including 37°C., no change in exchangeable manganese occurred when no crop residues were added to the soil. At 47°C., there was a small but significant increase in exchangeable manganese (table 3). This latter effect is in keeping with Fujimoto and Sherman's results (2).

To determine whether other sources of carbon and nitrogen for the soil micro-



organisms would affect the exchangeable manganese in the same way, glucose and peptone were incorporated in the soil at the same carbon and nitrogen levels, and the amended soil was incubated at 37°C. The same results were obtained, except that the peak was reached sooner and the rate of decrease of exchangeable manganese was also more rapid (table 4).

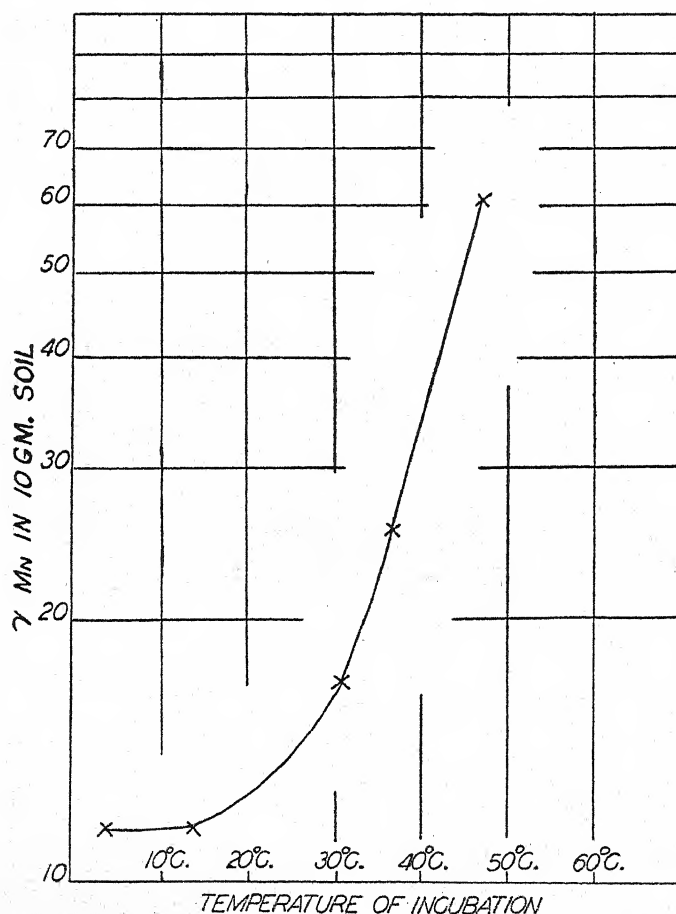


FIG. 1. EFFECT OF TEMPERATURE OF INCUBATION ON MAXIMUM MANGANESE VALUES OF MERRIMAC SANDY LOAM AMENDED WITH OAT STRAW AND ALFALFA MEAL

There was a difference of about 6γ exchangeable manganese per 10.0 gm. soil between the 0-day values of the soil amended with oat straw and alfalfa meal and the unamended control soil. This difference was probably the amount of soluble manganese in the crop residues. There was no effect of soluble components of the oat straw and alfalfa meal on the solubility of soil manganese, such as was reported for copper (3).

TABLE 2

*Effect of temperature of decomposition of organic matter (oat straw and alfalfa meal) on exchangeable manganese in Merrimac sandy loam*

INCUBATION  <i>days</i>	MICROGRAMS EXCHANGEABLE MANGANESE PER 10.0 GM. SOIL*				
	4°C.	14°C.	30°C.	37°C.	47°C.
0	6.9 ± 0.1	5.2 ± 1.0	5.2 ± 1.0	7.1 ± 0.7	6.7 ± 0.1
1	8.9 ± 0.7	10.0 ± 0.6	16.4 ± 0.4	21.6 ± 0	44.1 ± 1.5
2	11.7 ± 0.1	11.8 ± 0.6	15.3 ± 1.4	23.8 ± 1.6	59.8 ± 1.8
3	11.5 ± 0.1	11.5 ± 0.9	17.0 ± 0	25.6 ± 0.5	61.5 ± 0.8
4	13.4 ± 0.7	13.6 ± 1.0	16.1 ± 0.4	20.7 ± 0.4	61.6 ± 0.8
7	9.3 ± 0	11.6 ± 0.4	9.6 ± 0.6	12.7 ± 0.3	60.9 ± 0.6
14	6.7 ± 0.2	8.9 ± 0.3	4.5 ± 0.4	6.4 ± 0.6	34.8 ± 0.7
21	3.6 ± 1.4	5.3 ± 0.2	....	3.5 ± 0.7	25.7 ± 0.6

\* Average value and mean variation of duplicate samples.

TABLE 3

*Effect of temperature of incubation on exchangeable manganese in Merrimac sandy loam to which no organic matter was added*

INCUBATION  <i>days</i>	MICROGRAMS EXCHANGEABLE MANGANESE PER 10.0 GM. SOIL		
	30°C.	37°C.	47°C.
0	1.1	1.3	1.6
1	1.5	1.9	4.1
2	1.0	2.0	5.0
3	1.5	2.0	7.1
4	1.5	1.5	7.6
7	1.2	1.7	8.9
14	0.8	1.4	10.0
21	...	1.5	13.3

TABLE 4

*Effect of decomposition of organic matter (glucose and peptone) on exchangeable manganese in Merrimac sandy loam at 37°C.*

INCUBATION  <i>days</i>	MICROGRAMS EXCHANGEABLE MANGANESE PER 10.0 GM. SOIL	
	No organic matter added	Glucose and peptone added
0	1.2	1.9 ± 0.4
1	1.6	31.0 ± 1.8
2	2.0	27.7 ± 2.4
3	1.6	11.4 ± 1.2
4	1.7	7.2 ± 0.1
7	1.5	3.2 ± 0.2
14	1.8	2.1 ± 0.2

## DISCUSSION

There was no increase in exchangeable manganese when organic matter was not added to the soil. Consequently, the effect of temperature on the exchangeable manganese was a result of the effect on the decomposition of the plant residues. The increase of exchangeable manganese was probably not caused by the mineralization of the plant tissue, since the same effect was observed when soluble glucose and peptone were used to increase microbial activity. The increase of exchangeable manganese was probably caused by a reduction of the state of oxidation of the soil, brought about either by the removal of oxygen by microbial respiration more rapidly than it could be replaced from the atmosphere or by the production of reduced compounds, as a by-product of biological or nonbiological decomposition, which would have the same effect. The mechanism, however, is not a simple increase in soluble bivalent manganese, since water-soluble manganese did not increase during incubation at 37°C.

The decrease in exchangeable manganese, which commenced after the third day, was probably caused by the manganese-oxidizing bacteria, which have been shown to be very active in well-aerated soils in the pH range of 6.0 to 7.5 (5).

Since the increase in exchangeable manganese as a function of increasing incubation temperature becomes logarithmic above 30°C., the use of heat for complete or partial sterilization of soil should be further investigated. It is conceivable that toxic concentrations of manganese might result from the practice of steam sterilization of seedbeds and greenhouse soils. If the manganese-oxidizing bacteria were destroyed by heat, the decrease of the toxic concentrations of manganese by oxidation to the insoluble higher oxides would be prevented or markedly slowed down. Fujimoto and Sherman (2) found that steam sterilization increased exchangeable manganese in a number of soils from a few parts per million to about 3,000 p.p.m. Fifteen parts per million has been reported to be toxic to tobacco (1).

## SUMMARY

Merrimac sandy loam was amended with oat straw and alfalfa meal at a carbon-nitrogen ratio of 30 to 1 and a nitrogen level of 200 pounds per acre and incubated at 4°, 14°, 30°, 37°, and 47°C. The effect of temperature of incubation on the exchangeable manganese content was determined. The exchangeable manganese content increased to a maximum after about 3 days and then decreased to about the initial level after about 2 weeks' incubation. The rate of increase of exchangeable manganese for the first 3 days was a logarithmic function of temperature of incubation above 30°C. When glucose and peptone were substituted for oat straw and alfalfa meal, the effect on exchangeable manganese was similar except that the increase and subsequent decrease were more rapid.

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# EFFECT OF FUMIGATION, FERTILIZATION, AND VARIOUS OTHER SOIL TREATMENTS ON GROWTH OF ORANGE SEEDLINGS IN OLD CITRUS SOILS<sup>1</sup>

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It has been the experience of many California citrus growers that trees of a second or third planting in old groves do not grow so well as those of the first planting or as plantings of similar trees on soil that has never before been used for citrus. This condition is marked in some areas and occurs despite the fact that fertilizer, pest-control, and management practices are good; it is specific for citrus, as other crops will grow vigorously in old citrus soils.

When the underlying factors are not definitely understood, the phenomenon of poor growth of new plantings or reduced growth of old plantings in soils that are continuously cultivated to the same species is sometimes referred to as *Bodenmüdigkeit* (7) or "soil sickness." The usual method of controlling this condition has been to replant the species concerned in soil which has never been cropped to that species, or, when new land is lacking, to plant other crops.

In southern California reduced growth of citrus trees on old citrus soils is generally referred to as "slow decline of citrus." Inasmuch as citrus groves represent large investments, and as new land is scarce, it is vital to find, if possible, the causes of slow decline and to apply corrective measures.

Unsatisfactory growth of trees in soil previously cropped to the same species has been reported for several fruit varieties (7, 12, 14). Although many theories have been proposed (7), very little information is available concerning definite causes and methods of control. Theories commonly advanced to explain slow decline of citrus trees are the following:

*Nutritional deficiency.* Soil fertilization experiments in California (13) have indicated that growth of citrus is generally increased only by addition of nitrogen. Zinc, manganese, and sometimes copper deficiencies occur in certain areas, but these deficiencies may be controlled by nutritional sprays. It is possible, however, that citrus trees may in time deplete the available supply of other unknown or unrecognized essential elements.

*Nutritional unbalance.* Through continued use of various commercial fertilizers, it is possible that constituents which are only partly utilized by the plants may accumulate in the soil and thus create an unbalanced nutritional condition detrimental to subsequent growth.

*Deterioration of soil structure.* Prolonged use of certain fertilizer constituents (1) and excessive cultivation are known to bring about deterioration in the structure of some soils; this in turn may contribute to reduced growth of citrus trees.

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*Accumulation of toxic substances in the soil.* Certain plants excrete or leave toxic substances in the medium in which they grow (2, 3, 10). These substances may inhibit or reduce plant growth. It is possible that citrus roots excrete some toxic substance or contain a toxic material which is not destroyed or is only partly destroyed by the soil population. Eventually enough harmful substances of this nature may accumulate to affect tree growth adversely.

*Unfavorable microbial population of soil.* After many years of growth of citrus trees in the same soil, a microbial population may be built up which may be detrimental to plant growth in various ways. The principal biological agents in the soil possibly affecting citrus growth are nematodes, chiefly the citrus root nematode (*Tylenchulus semipenetrans* Cobb), pathogenic fungi and bacteria, and saprophytic soil microorganisms. The citrus root nematode has been isolated from many citrus areas throughout the world (4, 5, 15, 16). According to Thomas (16), severely infested trees always showed evidence of injury, whereas trees infested only slightly appeared normal. Pot experiments indicated that root and top development were retarded by the nematode. Foote and Gowans (5) are of the opinion that the citrus root nematode is to a large degree responsible for reduced growth of lemon trees on some of the soils of Ventura County, California. The citrus root nematode is found on the roots of both healthy and unhealthy trees, however, and inoculation experiments in South Africa (15) showed no deterioration of inoculated trees over the uninoculated.

Pathogenic fungi, primarily *Phytophthora* species, have been isolated from citrus roots. Inoculation experiments with these fungi resulted in injury or complete decay of the feeder roots (6, 8). The injury was found to be directly proportional to the moisture content of the soil. Klotz and Sokoloff (8) expressed the opinion that the importance of pathogenic fungi in the decline of citrus is conditioned by factors such as moisture content of the soil and presence of toxic substances, notably nitrite. Studies recently made by the author (9) on the qualitative nature of the fungus population of the root area of citrus trees indicate that growth of orange and lemon trees influences the nature of this population. The fungus most commonly found, a *Fusarium* sp., was consistently isolated from surface-sterilized citrus feeder roots. Nematode-infested roots were extensively permeated with this fungus. Rotting of feeder roots is very common in orchards where replants fail to grow vigorously.

In view of the increasing interest in the problems involved in replanting old citrus orchards, experiments were undertaken at this station to determine whether reduced growth could be demonstrated with citrus seedlings grown in old citrus soils in the greenhouse, and if so, to determine possible causes and methods of control. This report presents the results of 3 years of such experiments, 1945-1947.

#### MATERIALS AND METHODS

Old citrus soil was taken from groves which had supported citrus trees 40 to 70 years and in which citrus replants failed to grow normally. The soil was obtained by digging small holes to the desired depth under a sufficient number of trees to provide the quantity desired. Noncitrus soil was taken from adjacent areas which had never been cropped to citrus. All the noncitrus soils had been used for agricultural purposes at some time or were being cultivated at the time the soil was collected. For most of the studies reported here, the soils used were Ramona clay loam obtained near Whittier, California, or Yolo Sandy loam from the vicinity of Fullerton. The pH of both of these soils was approximately 7.0. A clay loam from La Verne, California (pH approximately 7.0), and a sandy loam for Santa Paula (pH approximately 8.0) were utilized to a lesser extent.

For all the experiments the soil was screened, mixed well, and placed in 3-gallon earthenware pots in 25-pound (dry-weight basis) lots. The fertilizer and organic residues used were mixed thoroughly with the soil in each container. Fumigants, where used, were placed near the bottom of the pot, and the soil surface was immediately moistened. In one experiment the soil was steam-sterilized by autoclaving at 15 pounds' pressure for 7 hours. In all cases, after fumigation or steam sterilization the soil was allowed to stand 4 to 6 weeks before being planted.

Unless otherwise stated, the amounts of the various materials added to the soil in the pots were as follows:

<i>Material</i>	<i>Amount per pot</i>
Ammonium sulfate ( $\text{NH}_4)_2\text{SO}_4$ .....	6 gm.
Treble superphosphate.....	2 gm.
Potassium chloride.....	1 gm.
Copper sulfate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ).....	0.028 gm.
Magnesium sulfate ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ).....	0.42 gm.
Manganese sulfate ( $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ ).....	0.084 gm.
Zinc sulfate ( $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ ).....	0.028 gm.
Boric acid.....	0.011 gm.
Agricultural minerals*.....	5 gm.
Organic residues (dry-weight basis).....	68 gm.
Carbon disulfide.....	12 ml.
Chloropicrin.....	4 ml.
Ethylene dibromide.....	2 ml.
Ethylene dichloride.....	20 ml.
D-D (dichloropropane and dichloropropylene mixture).....	8 ml.
Iscobrome (15 per cent methyl bromide and 85 per cent xylene) ..	8 ml.
Garden Dowfume (5 per cent ethylene dibromide in naphthylene) ..	12 ml.
Dithane (disodium ethylene bisdithio-carbamate), 1-1600 or 1-2400 dilution.....	Soil saturation
Hyamine (di-isobutyl phenoxy ethoxyethyl dimethyl benzyl ammonium chloride monohydrate), 1-1600 or 1-2400 dilution ..	Soil saturation

\* Agricultural minerals consist of a mixture of waste acid sludge and garbage incinerator ashes. The product contains small amounts of a large number of the minor plant-nutrient elements.

The amounts of fumigants applied were several times greater than those commonly used for control of nematodes in various vegetable crops (11), and were based on experience at the Limoneira and Sespe ranches near Santa Paula, California.

For the first of the studies, sour orange seeds were planted directly in the pots, and the developing plants were gradually thinned to three per pot. For the later studies, small sour or sweet orange seedlings were started in a compost consisting of sand, peat moss, and virgin soil. The compost mixture was washed from the roots before transplanting, and two seedlings were planted in each pot. All treatments were replicated five times.

Tomatoes were grown in some of the soils to test the general fertility level. Tomatoes were grown  $2\frac{1}{2}$  to 3 months and citrus seedlings 8 to 10 months before being harvested. After the plants were harvested, they were dried in the oven

at 70°C. and weighed to the nearest tenth of a gram. The average dry weight per pot was calculated for each treatment and is reported to the nearest gram in all the tables. In some of the studies the relative number of nematodes in the roots of citrus seedlings at harvest time was estimated by placing approximately 2 gm. of fresh roots in water, allowing them to stand approximately 6 hours, and then examining them under the microscope.

## RESULTS

The effect of fertilization and steam sterilization on the growth of tomato plants and of sour orange seedlings in soil from the Whittier district is recorded in table 1. The only marked response to nutrients occurred with nitrogen ad-

TABLE 1  
*Effect of fertilization and steam sterilization on growth of tomato plants and sour orange seedlings in old citrus and noncitrus soils from the vicinity of Whittier, California*

FERTILIZER TREATMENT	AVERAGE DRY WEIGHT PER POT								
	Tomato plants				Sour orange seedlings				
	Old citrus soil		Noncitrus soil		Old citrus soil		Noncitrus soil		Growth increase, noncitrus over old citrus (non-sterilized)
	Non-sterilized	Sterilized	Non-sterilized	Sterilized	Non-sterilized	Sterilized	Non-sterilized	Sterilized	
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	per cent
None (control).....	21	32	22	34	31	18	76	3	145
N.....	37	44	36	..	43	24	72	..	67
N, P.....	36	45	36	..	48	37	72	..	50
N, P, K.....	40	49	41	..	41	31	80	..	95
N, P, K, Mg, Cu, B, Mn, Zn.....	43	47	37	..	44	31	71	..	61
Alfalfa hay.....	44	51	47	..	41	27	75	..	83
Manure.....	..	..	..	..	39	18	75	..	92
Average.....	37	45	36	..	41	26	74	..	80

ditions. Other nutritional elements resulted in only slight additional growth, if any. Steam sterilization increased growth of tomato plants considerably, probably because of the increased liberation of nitrogen from the organic matter in the soil. The point to be stressed, however, is that there were no marked differences in the growth of tomatoes in the old citrus and noncitrus soils: the average dry weight of all the plants was approximately 37 gm. in the old citrus soil and 36 gm. in the noncitrus soil.

Results with sour orange seedlings planted in the same soils and given identical treatments were quite different (table 1). All the plants grew much better in the noncitrus soil than in the soil obtained from the old citrus orchards, the plants of all the treatments in the noncitrus soil averaging 80 per cent more growth than those in the old citrus soil.

Steam sterilization rendered both soils toxic to sour orange seedlings, as

evidenced by reduced growth. Even a year after sterilization, the soil in some of the pots was still toxic. As time went on, however, the retarded plants in certain containers began to grow in a sporadic manner; there was no apparent connection between growth and treatment. The toxic principal, whatever it was, evidently disappeared or was destroyed at different rates in the various pots.

Inasmuch as complete sterilization of the soil by the use of steam—a process calculated to destroy any adverse biological factors—left the soil toxic to citrus, the accomplishment of the same purpose by the use of various soil fumigants was attempted. All pots in these and succeeding studies were given nitrogen fertilizer so that lack of nitrogen might not be a growth-limiting factor.

TABLE 2

*Effect of soil fumigation on growth of sour orange seedlings in old citrus and noncitrus soils from the Whittier district\**

FUMIGATION TREATMENT	AVERAGE PLANT GROWTH PER POT				
	Old citrus soil		Noncitrus soil		Increase (+) or decrease (-), noncitrus over old citrus
	Dry weight	Difference due to fumigation	Dry weight	Difference due to fumigation	
	gm.	per cent	gm.	per cent	per cent
None (control).....	41	....	64†	....	+56
D-D.....	46	+12	50	-21	+9
Garden Dowfume.....	46	+12	45	-29	-2
Iscobrome.....	44	+7	39	-39	-11
Carbon disulfide.....	51	+25	54	-14	+6
Ethylene dichloride.....	47	+15	52	-17	+11

\* All pots received nitrogen fertilizer.

† Average of 20 replications.

The results of tests with soils from the Whittier district (table 2) show that all fumigants to a small degree stimulated growth of seedlings in the old citrus soil and depressed growth in the noncitrus soil. Apparently, not enough time was allowed between fumigation and planting for the fumigants to disappear entirely from this heavy clay loam soil. Beneficial action in the old soil was more than enough, however, to counterbalance the detrimental effect, and the net result was increased growth, although total growth was less than that in the untreated noncitrus soil. The poorest results were obtained with Iscobrome, and the best with carbon disulfide.

The influence of the same fumigants on growth of sour orange seedlings in Yolo sandy loam soil from the Fullerton district was also determined (table 3). Again, all the fumigants increased growth of the seedlings in the old citrus soil and either slightly decreased or increased growth in the noncitrus soil. The most favorable results were obtained with D-D, carbon disulfide, and ethylene dichloride, and the poorest with Iscobrome and ethylene dibromide (Garden



Dowfume). Growth of the seedlings was 116 per cent greater in the noncitrus-soil controls than in the old-soil controls. Although fumigation markedly increased growth of the seedlings in the old orchard soil, seedlings grown in the untreated noncitrus soil were still larger.

TABLE 3

*Effect of soil fumigation on growth of sour orange seedlings in old citrus and noncitrus soils from the vicinity of Fullerton, California\**

FUMIGATION TREATMENT	AVERAGE PLANT GROWTH PER POT				
	Old citrus soil		Noncitrus soil		Increase, noncitrus over old citrus
	Dry weight	Difference due to fumigation	Dry weight	Difference due to fumigation	
	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>per cent</i>	<i>per cent</i>
None (control).....	25	....	54	....	116
D-D.....	35	+40	63	+17	80
Garden Dowfume.....	32	+28	41	-24	28
Iscobrome.....	28	+12	40	-26	43
Carbon disulfide.....	38	+52	53	-2	40
Ethylene dichloride.....	36	+44	66	+22	83

\* All pots received nitrogen fertilizer.

TABLE 4

*Effect of soil fumigation and various other treatments on growth of sour orange seedlings in stored, air-dried old citrus soil from the Fullerton district\**

TREATMENT	AVERAGE DRY WEIGHT PER POT OF PLANTS	GROWTH DIFFERENCE DUE TO TREATMENT
	<i>gm.</i>	<i>per cent</i>
None (control).....	23	....
Soil waterlogged.....	6	-73
Carbon disulfide.....	49	+112
Carbon disulfide (soil waterlogged).....	15	-35
Ethylene dibromide.....	41	+80
Chloropicrin.....	53	+130
Dithane (1-1600).....	14	-39
Dithane (1-2400).....	17	-26

\* Soil stored in air-dry condition approximately 6 months before use. All pots received nitrogen fertilizer.

The influence of waterlogging, various fumigants, Dithane, and Hyamine on the growth of sour orange seedlings in old citrus soil from the Fullerton district was also studied. The soil was first air-dried and stored in bins for approximately 6 months, however, and larger seedlings were used than in other tests. The Dithane and Hyamine were added by bringing the soil up to moisture capacity with solutions of the chemicals. The fumigation treatments (table 4) stimulated plant growth more in the stored soil than in the fresh soil. Chloropicrin



was most effective and ethylene dibromide least. As noted below, storage of this soil in a dry condition apparently decreased subsequent growth of citrus seedlings. It is possible that some microbial factor in the old citrus soil is favored by drying and by storage for a certain time. Waterlogging greatly decreased growth in both untreated and fumigated soil, but seedlings in the fumigated waterlogged soil made approximately twice the growth of those in untreated waterlogged soil. Dithane decreased growth. Since Hyamine had no effect, results for this treatment are not recorded in the table.

The difference in growth of citrus seedlings in the old citrus and noncitrus soils from Fullerton was so great that additional lots of soil were obtained for further studies. One lot was taken from a depth of 12 to 24 inches, another from the same holes as the first but from a depth of 24 to 48 inches, and a third lot was taken from a depth of 12 to 48 inches. Tomatoes were grown in the first

TABLE 5

*Growth of tomato plants in old citrus and noncitrus soils from the Fullerton district*

SOIL	FERTILIZER TREATMENT	AVERAGE DRY WEIGHT PER POT OF PLANTS
		gms.
Old citrus		
12- to 24-inch depth.....	N	66
12- to 24-inch depth.....	N, P, K	69
12- to 24-inch depth.....	N, P, K, + agricultural minerals*	70
24- to 48-inch depth.....	N	59†
Noncitrus		
12- to 24-inch depth.....	N	71
24- to 48-inch depth.....	N	17†

\* See text for explanation.

† Plants phosphorus-deficient.

two lots of soil. As indicated in table 5, phosphorus, potassium, and trace elements added to the old citrus soil from the 12- to 24-inch depth did not increase growth materially. Dry weights of plants grown in the old citrus and noncitrus soils were similar. Growth was poor in both soils from the 24- to 48-inch depth, but was better in the old citrus soil. Plants in both soils from this depth showed marked symptoms of phosphorus deficiency.

Table 6 shows the effect of soil fumigation and fertilization on the growth of sour orange seedlings in soil from depths of 12 to 24 inches and 24 to 48 inches. Growth was not increased by additions of P, K, Mg, Cu, Mn, Zn, and B. Fumigation markedly increased growth in both soils, but much more in the noncitrus soil than in the old citrus soil. Examination of the roots in the noncitrus soil at harvest time indicated considerable rotting and regeneration of the roots, which were also teeming with nematodes. Apparently, some detrimental microbial factor in this lot of noncitrus soil prevented normal plant growth. Soil fumigation controlled this factor so that vigorous growth, characteristic of

that in noncitrus soil, resulted. The seedlings grew just as well in the fumigated noncitrus soil from the 24- to 48-inch depth as in that from the 12- to 24-inch depth. In the old citrus soil, however, much better growth occurred in the soil from the upper depth. Although fumigation greatly increased the growth of the seedlings in the old orchard soil, seedlings in the fumigated noncitrus soil were still larger.

The above lots of noncitrus soil were obtained near a pepper tree. In one other instance, as noted below, soil collected under a pepper tree was more responsive to soil fumigation than was adjacent old citrus soil. This is perhaps a coincidence, or it is possible that some microbial or other factors detrimental to citrus growth are favored by the growth of this tree.

TABLE 6

*Effect of soil fumigation and fertilization on growth of sour orange seedlings in old citrus and noncitrus soils from different depths in the Fullerton district\**

TREATMENT†	AVERAGE PLANT GROWTH PER POT IN SOIL FROM DIFFERENT DEPTHS									
	12-24 inches					24-48 inches				
	Old citrus		Noncitrus		Increase or decrease, noncitrus over old citrus	Old citrus		Noncitrus		Increase or decrease, noncitrus over old citrus
	Dry weight	Difference due to treatment	Dry weight	Difference due to treatment		Dry weight	Difference due to treatment	Dry weight	Difference due to treatment	
	gm.	per cent	gm.	per cent	per cent	gm.	per cent	gm.	per cent	per cent
None (control)...	18	....	14	....	-22	10	....	13	....	+30
Fumigation										
Carbon disulfide	27	+50	42	+200	+55	18	+80	41	+215	+128
Ethylene dichloride.....	29	+61	42	+200	+45	22	+120	42	+223	+91
Fertilization with										
P, K, Mg, Cu, Mn, B, Zn....	18	0	15	+7	-17	9	-10	12	-8	+33

\* Noncitrus soil obtained near pepper tree.

† All pots received nitrogen fertilizer.

Sweet orange seedlings were grown in soils from the 12- to 48-inch depth. The results (table 7) were similar to those obtained with sour orange seedlings. The plants grown in the old citrus soil did not respond to inorganic fertilizers and were stimulated but slightly by alfalfa hay. Soil fumigation doubled the yield in the old soil but only slightly stimulated growth in the soil virgin to citrus. The dry weight of seedlings in the check pots was 172 per cent greater in the noncitrus soil than in the old citrus soil. Again, as with the sour orange seedlings, although fumigation markedly increased growth in the old soil, plants in the noncitrus control pots were considerably larger (fig. 1).

Treatment of the Fullerton soil with certain insecticides and fungicides; namely, Zerlate, Fermate, Dithane, Hyamine, Phygon, and hexachlorocyclohexane, either killed the plants or reduced growth.

In table 8 data on growth of sour orange seedlings in old citrus and noncitrus soils from La Verne and Santa Paula, California, are compared. Growth was

TABLE 7

*Effect of soil fumigation and fertilization on growth of sweet orange seedlings in old citrus and noncitrus soils (12- to 48-inch depth) from the Fullerton district\**

TREATMENT	AVERAGE GROWTH PER POT OF PLANTS				
	Old citrus soil		In noncitrus soil		Increase, noncitrus over old citrus
	Dry weight	Increase due to treatment	Dry weight	Increase due to treatment	
	gm.	per cent	gm.	per cent	
None (control).....	11	..	30	..	172
Fumigation					
Carbon disulfide.....	20	82	35	16	75
Ethylene dichloride.....	19	73	34	13	79
Fertilization					
Alfalfa hay.....	14	27	..	..	..
P, K, Mg, Mn, B, Cu, and Zn.....	12	9	..	..	..

\* All pots received nitrogen fertilizer.

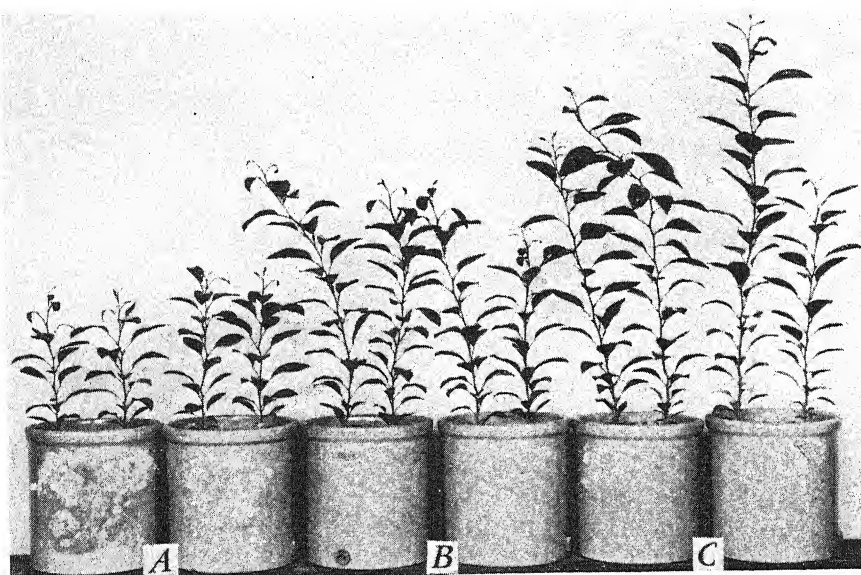


FIG. 1. SWEET ORANGE SEEDLINGS GROWING IN YOLO SANDY LOAM SOIL FROM THE VICINITY OF FULLERTON, CALIFORNIA

A, Old citrus soil; B, fumigated old citrus soil; C, non-citrus soil. All pots received nitrogen fertilizer

better in the noncitrus soil than in the old citrus soil from both areas. The noncitrus soil from Santa Paula was obtained under a pepper tree and was more

responsive to soil fumigation than the old citrus soil. The roots in the unfumigated pots at harvest time showed extensive rotting and regeneration; roots in the fumigated pots, on the other hand, appeared healthy.

TABLE 8

*Growth of sour orange seedlings in old citrus and noncitrus soils from the La Verne and Santa Paula districts\**

FUMIGATION TREATMENT	AVERAGE DRY WEIGHT PER POT OF PLANTS					
	La Verne soil			Santa Paula soil		
	Old citrus	Noncitrus	Increase, noncitrus over old citrus	Old citrus	Noncitrus†	Increase, noncitrus over old citrus
	gm.	gm.	per cent	gm.	gm.	per cent
None (control) .....	28	42	50	25	30	20
Carbon disulfide .....	..	..	..	34	47	38

\* All pots received nitrogen fertilizer.

† Soil obtained under pepper tree.

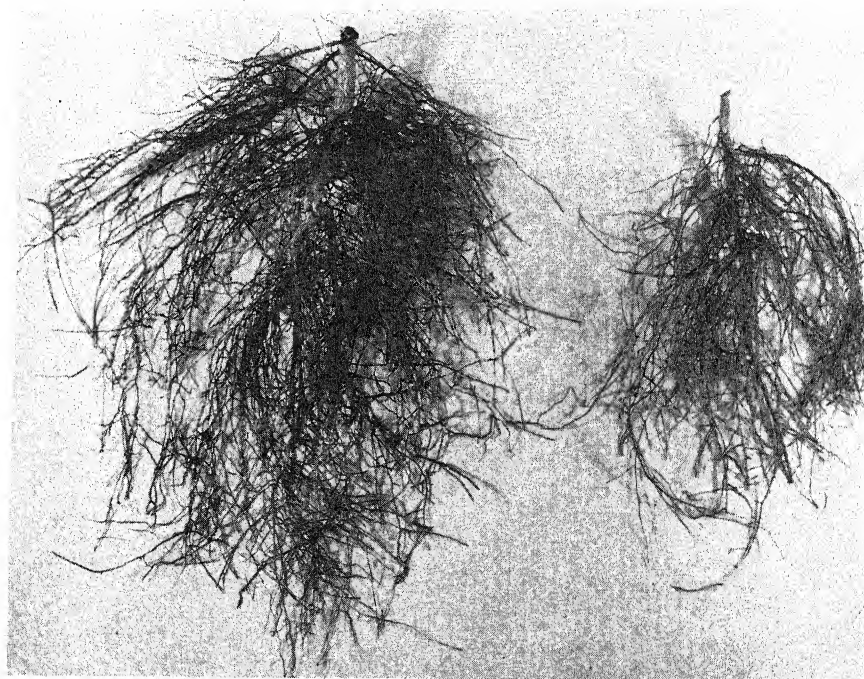


FIG. 2. ROOT GROWTH OF SWEET ORANGE SEEDLINGS GROWN IN NONCITRUS (LEFT) AND OLD CITRUS (RIGHT) SOILS FROM THE VICINITY OF FULLERTON, CALIFORNIA

The effect on plant growth of air-drying and storage of the soil previous to planting was also studied. Data in table 9 show that the growth of sour orange seedlings in soils from the Whittier district was, respectively, 76, 58, and 40

per cent greater in fresh noncitrus soil and in air-dried noncitrus soil after storage for 1 year and for 2 years, than in comparable fresh and stored old citrus soils. A similar comparison for fresh soils and for soils air-dried and stored for 1 year, from the Fullerton district, showed plant growth to be, respectively, 133 and 170 per cent greater in noncitrus soils than in old citrus soils. As previously pointed out, storage of the old citrus soil from Fullerton rendered it a less favorable medium for growth of citrus than the fresh soil: roots of seedlings in these pots were filled with citrus root nematodes and had undergone considerable decay. Apparently, some microbial factor is favored by drying and storage for a period up to at least 1 year. In the heavy Whittier soil, on the other hand, there were fewer nematodes in the roots in the stored old citrus soil than in the fresh soil, and the roots were in better condition.

TABLE 9  
*Effect of soil storage on growth of sour orange seedlings\**

SOIL SOURCE AND CONDITION AT TIME OF PLANTING	YEAR SEEDLINGS PLANTED†	AVERAGE DRY WEIGHT PER POT OF PLANTS		
		Old citrus soil	Noncitrus soil	Increase, noncitrus over old citrus
		gm.	gm.	per cent
Whittier district				
Fresh.....	1945	42	74	76
Stored (air-dried) 1 year.....	1946	41	65	58
Stored (air-dried) 2 years.....	1947	30	42	40
Fullerton district				
Fresh.....	1946	25	54	116
Fresh.....	1947	18	42	133
Stored (air-dried) 1 year.....	1947	14	38	170

\* All pots received nitrogen fertilizer.

† Seedlings grown 8 to 10 months.

As shown in figure 2, growth of the root systems of the orange seedlings roughly paralleled that of the tops.

At the time of harvest, all the roots of the citrus seedlings growing in the unfumigated old citrus soils harbored citrus root nematodes. Relative numbers of nematodes varied, roots in the soil from Whittier containing the least and those in the soil from Santa Paula the most. Roots of seedlings growing in most noncitrus soils contained very few or no nematodes. Although no citrus nematodes could be found in the noncitrus soil obtained near pepper trees, the roots of orange seedlings growing in these soils were literally teeming with these organisms at harvest time. In the majority of trials, soil fumigation prior to planting effectively controlled nematodes; they were found in only a few isolated pots when the plants were harvested.

Noncitrus soils and fumigated old citrus soils in which sour orange seedlings were growing were inoculated at 2-month intervals with approximately 500-ml.



doses of water extracts of fresh old citrus soils to determine whether any biological factor could be transferred to the noncitrus or fumigated old citrus soils. Inoculation in this manner did not materially influence growth in either soil (table 10). Examination of the roots of the seedlings at the end of the growth period, and of the fungus flora of the soil, showed that inoculation with old soil

TABLE 10

*Effect of inoculation\* of noncitrus and fumigated† old citrus soils with water extracts of fresh noncitrus and old citrus soils on growth of sour orange seedlings*

SOIL	SOIL TREATMENT‡	AVERAGE DRY WEIGHT PER POT OF PLANTS
		<i>gm.</i>
Noncitrus Whittier district	None (control)	63
	Inoculation with old citrus soil from Fullerton district	63
	Inoculation with old citrus soil from Whittier district	64
	Inoculation with noncitrus soil from Whittier district	67
Fullerton district	None (control)	52
	Inoculation with old citrus soil from Fullerton district	49
	Inoculation with old citrus soil from Whittier district	46
	Inoculation with noncitrus soil from Fullerton district	56
Old citrus Fullerton district	None (control)	18
	Fumigation	27
	Fumigation and inoculation with old citrus soil from Fullerton district	26
	Fumigation and inoculation with fungus flora of old citrus soil from Fullerton district	27
Santa Paula district	None (control)	25
	Fumigation	34
	Fumigation and inoculation with old citrus soil from Santa Paula district	34

\* Inoculations were made with water extracts of fresh soil at 2-month intervals for 8 months.

† Fumigation was with carbon disulfide.

‡ All pots received nitrogen fertilizer.

had not altered the fungus population of the soil to any appreciable extent or increased the number of nematodes in the roots.

#### DISCUSSION

Sour and sweet orange seedlings made approximately 50 to 175 per cent more growth in soil from areas which had never been cropped to citrus than in soil from adjacent areas which had supported citrus trees 40 to 70 years. This confirms the observation of many citrus growers and others who have noticed

that trees of a second or third planting of citrus in old groves do not grow so well as those of the original planting or so well as plantings of similar trees on noncitrus soils. The fact that this condition can be demonstrated in the greenhouse with seedlings makes it possible to conduct exploratory experiments concerning causes and remedies, and thus to save the great amount of time involved in extensive field experiments.

Additions to the soil of plant nutrients, except nitrogen, failed to increase growth of orange seedlings. This is in general harmony with field observations. Nitrogen was therefore added to the soil of all pots in the present experiments so that lack of this nutrient might not be a growth-limiting factor.

Tomato plants grew as well in old citrus soil as in soil virgin to citrus. In both soils, in 3-gallon pots, plants grew almost to the greenhouse ceiling (4 to 5 feet) before deficiency symptoms became obvious. This indicates that the soils used were very fertile.

It appears that the cause of reduced growth of orange and lemon trees in old citrus soil is specific for citrus and is probably not the result of any common nutrient deficiency. The possibility is not excluded, however, that the available supply of some trace element required by citrus and not by other plants is used up in time and causes reduced growth thereafter.

In every test, fumigation of old citrus soils prior to planting stimulated growth of orange seedlings, and in some soils growth was doubled. In view of the fact that lack of plant nutrients was not a limiting factor, the marked stimulation of growth in the old citrus soils cannot be adequately explained on the basis of an increased nutrient supply resulting from the partial sterilization of the soil by the fumigants. Nematodes and root rotting were, in the main, effectively controlled by fumigation. (In a few fumigated pots pathogenic fungus infections were followed by an increase in nematode populations.) The results indicate that microbial factors, possibly nematodes and fungi, are at least partly responsible for reduced growth in second and third citrus plantings. In every experiment, however, growth of seedlings in fumigated old citrus soil was not so great as that in noncitrus soils in which no detrimental microbes were present. This point is well illustrated in table 11.

Fumigation of the old citrus soil prior to planting either controlled or greatly reduced the incidence of nematodes and possibly of other microbial factors in the roots and soil and resulted in marked stimulation of growth, although it did not increase growth to a point comparable to that possible in noncitrus soil. This strongly suggests that factors other than microbial contribute to poor growth of citrus trees in soil in which oranges, lemons, or grapefruit have been grown for a long time. This conclusion is further confirmed by the fact that the roots of most seedlings grown in pots of unfumigated old citrus soil in the greenhouse contained fewer nematodes than the roots of trees growing in the orchard where the soil was obtained.

Although it is possible that some detrimental organisms which are not destroyed by heavy fumigation are present in the soil, or that the available supply of some unrecognized but essential trace element is used up, these studies suggest

that some toxic material may be partly responsible for the reduced growth of citrus in old citrus soils. Such a hypothetical toxic substance could originate either from the roots themselves or from organisms decomposing root excretions and dead root material.

Concerning the detrimental microorganisms, it may be asked whether nematodes or other organisms are partly the cause of reduced plant growth, or whether other factors weaken the plant or in other ways favor the building up of an adverse microbial population, which then causes further damage. The inoculation experiments indicate that inoculation of noncitrus soil and of fumigated old citrus soil during a 9 months' growing period did not result in the establishment of citrus root nematodes and of the fungus population of the inoculum. On the

TABLE 11  
*Nematode population of roots and growth of citrus seedlings\* in several California soils†*

SOURCE OF SOIL	AVERAGE DRY WEIGHT PER POT OF PLANTS				NEMATODE POPULATION‡			
	Old citrus soil		Noncitrus soil		Old citrus soil		Noncitrus soil	
	Unfumi- gated	Fumi- gated§	Unfumi- gated	Fumi- gated§	Unfumi- gated	Fumi- gated§	Unfumi- gated	Fumi- gated§
	gm.	gm.	gm.	gm.				
Fullerton district								
3- to 18-inch depth.....	25	38	54	..	+	-	-	..
12- to 24-inch depth.....	18	27	..	42	++	-	..	-
24- to 48-inch depth.....	10	18	..	41	++	-	..	-
12- to 48-inch depth¶.....	11	20	30	..	++	+	-	..
Whittier district								
3- to 18-inch depth.....	41	51	64	..	+	-	-	..
Santa Paula district								
12- to 48-inch depth.....	25	34	..	47	+++	-	..	-

\* Sour orange seedlings used in all experiments, except as specified.

† All pots received nitrogen fertilizer.

‡ Explanation of symbols: - = <1 nematode per gram of roots; + = present in small numbers; ++ = present in moderate numbers; and +++ = present in large numbers.

§ Fumigated with carbon disulfide.

¶ Sweet orange seedlings were used in this experiment.

other hand, through natural inoculation, or by carry-over from seedlings, the nematodes and certain fungi, mainly a *Fusarium* sp. characteristic of old citrus soils (9), rapidly became established in the noncitrus soils taken from under pepper trees. It appears that either some factor in the soil made the plants susceptible to these organisms, or the soil was in a favorable condition for their rapid development. The increased growth of citrus seedlings after soil fumigation could conceivably result from the complete or partial destruction of certain toxic substances which either weaken the plant or in other ways make conditions favorable for detrimental organisms.

Any condition unfavorable to the growth of the citrus plant would render it more susceptible to other adverse factors. Thus the healthy tree may be resistant to certain weakly pathogenic fungi, whereas a toxic substance, nema-

todes, poor aeration, heavy insect infestation of the tops, or other factors, may so weaken the tree that it is no longer resistant to the fungi. Undoubtedly several interrelated factors cause reduced growth of citrus in soils which have supported growth of the same species for long periods. Some of these factors are primary in nature and others are secondary.

#### SUMMARY

Sour and sweet orange seedlings grown in 3-gallon pots in the greenhouse made approximately 50 to 175 per cent more growth in noncitrus soil, that is, in soil from areas which had never been cropped to citrus, than in old citrus soil from adjacent areas which had supported citrus trees 40 to 70 years. Seedlings in old citrus soils did not respond to applications of P, K, Mg, Cu, B, Zn, or Mn.

Soil fumigation prior to planting usually controlled root rotting and the citrus root nematode (*Tylenchulus semipenetrans* Cobb) and markedly stimulated growth of sour and sweet orange seedlings in old citrus soil. In most noncitrus soils growth was only slightly increased or decreased by fumigation. Noncitrus soils taken from areas under or near pepper trees produced poor growth of citrus seedlings, but fumigation of these soils prior to planting restored the vigorous growth characteristic of that in most noncitrus soils. Applications of soil fumigants markedly stimulated growth of sour and sweet orange seedlings in old citrus soil but did not increase growth to a point comparable to that of plants in untreated or fumigated noncitrus soil.

Although microbial factors are probably partly responsible for the reduced growth of trees of a second or third planting of citrus in old orchards, other factors, such as the presence of some toxic material, may also be involved. Inoculation of noncitrus soil with water extracts of old citrus soil did not reduce growth of citrus seedlings or result in the establishment of the citrus root nematode or of the fungus population of the old soil during a 9 months' growing period.

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# EFFECT OF CATION-EXCHANGE PROPERTIES OF SOIL ON THE CATION CONTENT OF PLANTS<sup>1</sup>

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Knowledge of the cation content of plants is essential to estimating the amounts of mineral elements removed from the soil. It is helpful also as a means of determining the possible mechanism involved in the uptake of mineral elements from the soil. When a detailed chemical characterization of soils is available, the relationships between cation content of plants and exchange properties of soils can be studied. In the present investigation the effects of cation-exchange capacity, Ca-Mg and Ca-K ratios, and  $\text{NaNO}_3$  additions on the cation content of soybeans, oats, and turnips and on the release of cations have been studied. Comparisons have been made between the cation contents of these plants and the amounts and ratios of these cations that can be extracted with small amounts of HCl in the laboratory.

## MATERIALS AND METHODS

### *Soil and cultural methods for soybeans*

The soil used was Portsmouth fine sandy loam from the Coastal Plain area of North Carolina. It consists primarily of sand and organic matter, the exchange properties being, therefore, those of an organic type colloid. The exchange capacity was 20.8 m.e., 96 per cent of which was H. The treatment involved addition of  $\text{Ca}(\text{OH})_2$ , to give a constant degree of Ca saturation, and three levels each of Mg and K. Two thirds of the desired amount of soil was placed in a rotating mixer, then  $\text{Ca}(\text{OH})_2$  and  $\text{MgCO}_3$  were added in suspension to give a thin paste. After this mixed for 15 minutes, a mixture of KOH and  $\text{H}_3\text{PO}_4$  in solution was supplied and the suspension mixed again. The remaining third of soil was then added and the mixing continued for 30 minutes. The mix, which now was a soft paste, was allowed to stand overnight, mixed again, and transferred into large metal trays. After the soil had dried, it was screened. Part of the soil was then mixed with an equal portion of pure sand, and another part was mixed with three portions of sand. This provided for a total of 30 individual treatments. Samples of the undiluted soils were analyzed for cation-exchange capacity, exchangeable H, Ca, Mg, and K according to the  $\text{BaCl}_2$ -triethanolamine procedure (14). The results of this analysis are shown in table 1.

Four 16-pound portions of the soil or soil-sand mixtures of each treatment were weighed into 2-gallon glazed pots. On May 7, 1946, the pots were seeded with soybeans (variety Ogden), and after 10 days the plants were thinned to four per pot. On June 24, at the beginning of the blooming stage, the tops of

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TABLE 1  
Cations in soil and in soybean tops, and dry weights of soybean tops

TREAT- MENT	CATIONS IN SOIL			CATIONS IN SOYBEANS (FIRST HARVEST)				CATIONS IN SOYBEANS (SECOND HARVEST)				DRY WEIGHTS OF SOYBEANS  gm.
	Ca	Mg	K	Ca	Mg	K	Sum	Ca	Mg	K	Sum	
	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	
Cation-exchange capacity—20.8 m.e.												
1	8.3	0.56	0.225	69.9	32.4	47.9	150	67.7	30.9	33.7	132	17.7
2	8.3	0.56	0.410	65.1	28.8	54.8	149	60.9	27.9	41.7	131	20.4
3	8.3	0.56	0.820	62.0	26.3	64.7	153	54.8	24.8	55.8	135	17.9
4	8.3	0.88	0.196	67.1	35.5	39.3	142	69.5	38.1	27.0	135	19.3
5	8.3	0.88	0.396	60.3	32.1	56.5	150	58.8	30.1	49.0	138	16.3
6	8.3	0.88	0.994	48.7	28.3	74.7	152	49.9	25.2	65.0	140	17.7
7	8.3	1.68	0.188	67.6	44.3	32.4	144	66.8	49.6	20.9	137	18.7
8	8.3	1.68	0.412	57.6	34.6	55.5	148	54.9	34.1	40.4	130	20.7
9	8.3	1.68	0.808	51.1	29.1	69.5	150	50.2	28.3	55.3	134	21.0
10	8.3	0.30	0.080	92.0	36.9	15.3	144	87.5	36.1	8.8	133	20.0
Cation-exchange capacity—10.4 m.e.												
11	4.2	0.28	0.113	69.1	29.1	47.7	146	68.7	30.0	25.8	125	12.3
12	4.2	0.28	0.205	67.7	27.8	46.8	142	65.8	28.4	37.4	131	14.2
13	4.2	0.28	0.410	61.9	27.4	69.1	158	56.8	26.1	55.6	139	13.4
14	4.2	0.44	0.098	75.7	37.3	37.2	150	69.6	37.6	23.2	130	14.4
15	4.2	0.44	0.198	62.6	30.5	54.2	147	61.0	31.3	40.4	133	15.1
16	4.2	0.44	0.497	52.0	25.9	70.7	149	50.1	26.8	58.1	135	14.9
17	4.2	0.84	0.094	68.2	48.8	28.5	146	63.5	47.2	17.2	128	17.5
18	4.2	0.84	0.206	56.4	34.4	53.9	145	57.9	34.6	38.2	131	16.5
19	4.2	0.84	0.404	50.7	31.5	66.7	149	50.6	29.6	53.4	134	15.5
20	4.2	0.15	0.040	95.5	37.5	17.6	151	91.3	32.5	9.3	133	13.4
Cation-exchange capacity—5.2 m.e.												
21	2.1	0.14	0.056	83.4	32.9	41.6	158	79.1	30.7	26.3	136	9.1
22	2.1	0.14	0.102	72.7	30.2	41.3	144	67.6	27.6	29.2	124	10.1
23	2.1	0.14	0.205	66.6	27.4	60.7	155	56.8	26.6	45.4	129	10.5
24	2.1	0.22	0.049	77.7	37.2	23.1	148	71.2	38.1	19.1	128	10.2
25	2.1	0.22	0.099	65.2	33.5	40.2	139	63.2	33.5	30.5	127	11.9
26	2.1	0.22	0.248	59.1	28.3	62.4	150	53.5	26.3	49.8	130	12.1
27	2.1	0.42	0.047	71.9	47.8	31.8	152	66.2	49.3	15.3	131	11.2
28	2.1	0.42	0.103	61.5	36.6	38.1	136	61.9	37.7	30.8	130	11.5
29	2.1	0.42	0.202	55.9	33.3	52.5	142	53.9	30.9	41.3	126	13.2
30	2.1	0.08	0.020	96.2	31.6	11.4	139	84.3	26.9	9.5	121	9.4

two plants were harvested. The final harvest was made at the stage when pods had formed, on July 19. The soybean tops were dried, ground, and analyzed for Ca, Mg, and K.

*Soil and cultural methods for oats and turnips*

Following the soybean experiment, the soil was screened, the roots were removed, and the four replications for each of the 30 treatments were composited.

Samples for analysis were taken. The results are shown in table 2. For each treatment six 8-pound portions were weighed into 1-gallon pots. On January

TABLE 2

*Cations in soil and in oats and turnip tops, and dry weights of oats and turnip tops*

TREAT- MENT	CATIONS IN SOIL			CATIONS IN OATS					CATIONS IN TURNIPS					DRY WEIGHT	
	Ca	Mg	K	Ca	Mg	K	Na	Sum	Ca	Mg	K	Na	Sum	Oats	Turn- ips
	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	gm.	gm.
<i>Cation-exchange capacity—20.8 m.e.</i>															
1	7.9	0.40	.102	26.4	25.3	18.9	62.1	133	157.8	39.6	17.2	30.6	245	11.8	9.3
2	7.9	0.40	.211	23.1	22.8	31.0	56.9	134	143.1	32.2	25.0	21.0	221	11.1	9.3
3	7.9	0.40	.623	19.3	22.9	46.0	25.9	114	128.6	26.2	52.5	12.5	220	11.4	11.3
4	7.9	0.70	.094	21.4	27.5	14.4	77.5	141	154.2	47.9	15.3	47.0	264	11.9	9.5
5	7.9	0.70	.203	19.2	26.0	35.8	53.5	135	144.5	42.6	28.6	18.6	234	10.9	9.8
6	7.9	0.70	.674	18.1	23.1	51.8	23.1	116	130.4	28.3	76.1	11.1	246	11.1	10.3
7	7.9	1.43	.097	20.8	32.7	17.0	76.0	147	146.8	54.7	17.9	34.1	254	10.2	10.3
8	7.9	1.43	.212	18.1	29.0	32.4	56.2	136	136.3	52.6	27.9	21.3	238	11.8	10.7
9	7.9	1.43	.591	16.0	26.5	49.9	28.0	120	117.5	40.6	45.1	12.7	216	10.5	10.1
10	7.9	0.17	.053	26.5	21.0	12.2	89.1	149	151.0	27.2	14.2	67.3	260	9.1	8.5
<i>Cation-exchange capacity—10.4 m.e.</i>															
11	3.8	0.16	.061	20.1	17.8	15.7	82.0	136	146.7	30.0	13.6	77.6	268	8.6	7.7
12	3.8	0.16	.093	17.9	20.1	20.9	71.8	131	150.4	33.0	21.3	45.5	250	9.0	7.2
13	3.8	0.16	.222	15.4	19.9	42.2	38.0	116	128.4	23.8	41.4	32.2	226	8.1	6.6
14	3.8	0.31	.053	18.8	22.4	15.6	70.2	127	147.8	38.5	20.1	42.8	249	8.0	7.0
15	3.8	0.31	.086	18.3	22.4	23.4	73.9	133	157.8	38.7	21.5	30.6	249	8.0	6.2
16	3.8	0.31	.314	13.8	18.4	49.0	27.8	109	125.5	30.0	56.6	19.0	231	8.3	7.8
17	3.8	0.69	.062	16.0	26.1	14.7	79.8	137	148.2	54.1	13.9	59.7	276	7.3	6.7
18	3.8	0.69	.085	15.8	23.3	23.6	63.3	126	133.8	53.3	18.0	34.7	240	7.7	7.2
19	3.8	0.69	.221	12.6	22.8	43.9	44.8	124	122.2	27.3	46.3	32.3	242	7.3	6.4
20	3.8	0.10	.032	22.4	17.0	13.6	90.6	144	180.2	27.9	14.0	80.3	302	7.0	4.6
<i>Cation-exchange capacity—5.2 m.e.</i>															
21	1.9	0.07	.036	18.4	22.4	13.1	89.6	144	147.1	32.4	11.5	73.5	265	6.9	5.9
22	1.9	0.07	.054	13.1	19.3	18.7	73.2	124	146.4	25.8	14.1	58.0	244	7.2	5.2
23	1.9	0.07	.113	11.2	17.6	33.5	54.6	117	140.8	22.0	17.2	34.0	214	6.2	6.0
24	1.9	0.13	.032	16.4	25.1	14.9	89.5	146	155.5	36.7	12.1	75.8	280	5.0	4.8
25	1.9	0.13	.055	13.4	22.3	19.6	82.5	138	134.9	29.7	14.8	47.9	227	6.3	4.6
26	1.9	0.13	.157	11.3	21.4	46.7	54.3	134	103.5	25.3	29.2	31.2	189	6.2	5.7
27	1.9	0.31	.038	13.4	24.0	18.3	79.6	135	155.2	40.5	16.8	60.7	273	5.3	4.3
28	1.9	0.31	.054	11.9	22.8	15.5	69.6	120	135.6	49.0	17.8	64.0	266	6.8	5.4
29	1.9	0.31	.103	10.3	22.3	31.6	71.1	135	108.4	31.3	22.1	39.2	201	5.4	4.9
30	1.9	0.04	.021	15.1	17.5	15.8	89.1	138	183.0	27.0	12.7	81.5	304	6.0	3.2

28, 1947, 0.225 gm.  $\text{NaNO}_3$  (equivalent to 1 mgm. N per 100 gm. soil) and 0.034 gm.  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$  (equivalent to 0.01 m.e. Mn per 100 gm. soil) were added in solution. The following day three pots for each treatment were seeded with oats (variety Victorgrain) and three with turnips (variety Seven Top). After 8



days the oats were thinned to eight plants and the turnips to four plants per pot. On February 19 and at weekly intervals thereafter, 0.225-gm. portions of  $\text{NaNO}_3$  were added in solution. A total of six portions was supplied, providing 6 mgm. N or 0.43 m.e. Na per 100 gm. soil. The outer leaves of turnips were removed on March 29. The aerial parts of oats and turnips were harvested on April 23 and 26 respectively. The oat and turnip tops were dried, weighed, and analyzed for Ca, Mg, K, and Na.

The methods of plant analysis were essentially those of the A. O. A. C. (4) with slight modifications. Sodium was determined by the method outlined by Peech (17) with such changes as were necessary to make it suitable for use on plant materials. Release of cations from the soil by HCl (to supply 1 m.e. H) was measured as described before (13). Briefly, this involved shaking 40 gm. of soil with 200 ml. of 0.002 *N* HCl and determining the replaced cations in the filtrate.

### RESULTS

The Ca, Mg, and K contents of soybean tops produced at the various levels of exchangeable Ca, Mg, and K and at three cation-exchange capacities are shown in table 1. The dry weights of the second harvest stage of soybeans are also given. The data pertaining to the effect of cation-exchange properties on the growth and cation content of oats and turnip tops are presented in table 2. These data may be considered together since many relationships are common to both experiments. The dry weights of soybeans and oats were not affected by treatment within a cation-exchange capacity level. In the case of turnips, treatments 10, 20, and 30, which received no Mg or K additions, were definitely lower yielding. In all crops, the weights decreased significantly with decreasing cation-exchange capacity.

The principal effects of exchangeable cations on the cation content of soybeans, oats, and turnips are as follows: 1. Increasing the exchangeable K, for any given level of Mg and Ca, increases K and decreases Ca and Mg in the plants (and also decreases Na in the oats and turnips); 2. Increasing exchangeable Mg, for any given level of K and Ca, increases Mg, decreases Ca, and has no significant effect on K (and Na) in the plants, except that it causes a decrease in the K content of soybeans at the lowest K level; 3. For approximately the same level of exchangeable K, the K content of the plants increases and the Ca, Mg (and Na) content decreases with decreasing cation-exchange capacity; 4. Though the sum of the cations in the plant varies somewhat with the harvest or with the crop, it is relatively constant for each crop. The sum is not affected by exchange capacity in oats or soybeans, but with turnips there is a tendency toward a lower sum of cations with lower exchange capacities; 5. For any given soil treatment, the K content in oats and turnips is of about the same order. Ca and Mg are lower and Na higher in oats than in turnips.

#### *Proportionate amounts of cations taken up by plants*

A measure of the proportionate amounts of cations removed by plants is obtained by comparing the cation ratios of the plants with those in the soil. Such

data are shown for soybean tops in table 3 and for oats and turnip tops in table 4. To facilitate inspection of the data, the averages for similar Mg levels and K levels in soil are given. This procedure is justified, since the ratios within each group were not significantly different, although the Ca-K ratios in the plants were generally slightly lower with the higher Mg level in the soil. The Ca:Mg averages consist of treatment 1, 2, 3; 4, 5, 6, etc., and the Ca:K averages consist of treatment 1, 4, 7; 2, 5, 8, etc. (see tables 1 and 2).

TABLE 3  
*Cation ratios of soil and of soybean tops*

CATION RATIOS						COEFFICIENTS*			
Soil		Soybeans				First harvest		Second harvest	
Ca-Mg	Ca-K	First harvest		Second harvest		cMg	cK	cMg	cK
		Ca-Mg	Ca-K	Ca-Mg	Ca-K				
Cation-exchange capacity—20.8 m.e.									
4.7	9.5	1.7	0.8	1.6	0.9	2.8	11.9	2.9	11.6
9.5	20.4	1.8	1.1	1.9	1.4	5.3	18.5	5.0	14.6
16.2	42.8	2.3	1.8	2.2	2.6	7.0	23.8	7.4	16.5
25.2	96.4	2.5	6.0	2.4	9.9	10.1	16.1	10.5	9.7
Cation-exchange capacity—10.4 m.e.									
4.7	9.5	1.5	0.8	1.6	1.0	3.1	11.9	2.9	9.5
9.5	20.4	2.0	1.2	1.9	1.6	4.7	17.0	5.0	12.8
16.2	42.8	2.4	2.0	2.3	3.1	6.8	21.4	7.0	13.8
25.2	96.4	2.5	5.4	2.8	9.8	10.1	17.8	9.0	9.8
Cation-exchange capacity—5.2 m.e.									
4.7	9.5	1.7	1.1	1.5	1.2	2.8	8.5	3.1	7.9
9.5	20.4	2.1	1.7	1.9	2.1	4.5	12.0	5.0	9.7
16.2	42.8	2.4	2.6	2.4	3.7	6.8	16.5	6.8	11.7
25.2	96.4	3.0	8.4	3.1	8.9	8.3	11.5	8.1	10.8

\* The coefficient is obtained by dividing the Ca-Mg or Ca-K ratio of the exchangeable cations of the soil by the Ca-Mg or Ca-K ratio in the plant, and is designated as cMg or cK.

The results show that with increasing Ca-Mg or Ca-K ratios in the soil these ratios in the plants increase also. The cation ratios in the plants are in all cases smaller than those of the soil. This indicates that the plants have taken up proportionately more Mg or K than Ca. The significance of these interactions is more easily seen by dividing the Ca-Mg or Ca-K ratio of the plants into the Ca-Mg or Ca-K ratios of the soil. These coefficients, designated as *c* values, are also shown in tables 3 and 4. The cMg and cK values thus obtained yield a measure of the complementary ion effect. If this principle is operating, these coefficients should be expected to be relatively constant. In the soybean experiment, the Ca-Mg ratios in the soil range from 4.7 to 25.2, corresponding to a 5.4-fold increase. With respect to cMg this increase corresponds to 3.6-fold for the 20.8 m.e. series and about 2.8-fold for the 5.2 m.e. series. This



indicates a moderate complementary ion effect between Ca and Mg. The Ca-K ratios of the soil show a 10-fold increase but less than 2-fold for the cK values, hence, a strong complementary ion effect is indicated. This effect is somewhat greater for the second harvest and for the lower cation-exchange capacity level.

The complementary ion effect between Ca:Mg and Ca:K in oats and turnips is of about the same magnitude as in that mentioned for soybeans. There is some interaction between Ca and Mg and a strong complementary ion effect between Ca and K. The order of the cMg and cK values is turnips < soybeans < oats. The cation-exchange capacity does not consistently affect the cMg

TABLE 4  
*Cation ratios of soil and of oat and turnip tops*

CATION RATIOS						COEFFICIENTS*			
Soil		Oats		Turnips		Oats		Turnips	
Ca-Mg	Ca-K	Ca-Mg	Ca-K	Ca-Mg	Ca-K	cMg	cK	cMg	cK
<i>Cation-exchange capacity—20.8 m.e.</i>									
5.3	12.7	0.6	0.3	2.7	2.3	8.8	42.4	2.0	5.5
11.7	38.6	0.8	0.6	3.7	5.2	14.6	64.4	3.2	7.4
20.5	86.7	0.9	1.4	4.6	9.2	22.8	61.9	4.5	9.4
43.5	148.0	1.3	2.2	5.6	10.6	33.5	67.2	7.8	14.0
<i>Cation-exchange capacity—10.4 m.e.</i>									
5.3	15.6	0.6	0.3	3.2	2.7	8.8	52.0	1.7	5.8
12.5	46.1	0.8	0.8	4.0	7.2	15.6	57.6	3.1	6.4
25.3	69.3	0.9	1.2	5.0	9.6	28.1	57.8	5.1	7.2
37.0	123.3	1.3	1.6	6.5	12.9	28.4	77.0	5.7	9.6
<i>Cation-exchange capacity—5.2 m.e.</i>									
5.5	16.1	0.5	0.3	3.5	5.5	11.0	53.7	1.6	2.9
14.0	36.7	0.6	0.7	4.2	9.0	23.3	52.5	3.3	4.1
29.6	59.0	0.7	1.1	5.5	11.7	42.3	53.6	5.4	5.0
45.0	90.0	0.9	1.0	6.8	14.4	50.0	90.0	6.6	6.2

\* See footnote, table 3.

values, whereas the cK values decrease with decreasing exchange capacity, particularly in turnips.

In the experiment with oats and turnips constant amounts of  $\text{NaNO}_3$  were applied. The effect of Na on the composition of these plants was shown in table 2. The Na content of these plants was seen to be strikingly influenced by the exchangeable K of the soil. The extent of this interaction may be seen from a comparison between Ca-Na and K-Na ratios of the soil and in the plants. These results together with the cNa values are shown in table 5. With a constant Ca-Na ratio in the soil, the Ca-Na ratios in the plants tend to increase with increasing K-Na ratios of the soil, notably in turnips at the higher cation-ex-

change capacity. With decreasing cation-exchange capacity the Ca-Na ratios in the plants decrease, but to a lesser degree than in the soil. The plants, therefore, absorbed proportionately less Na than Ca from the soils of lower exchange capacity. Turnips contained, in all cases, less Na than Ca as compared with oats.

The results in table 5 show a direct relationship between the K-Na ratios of soil and those of plants. From K-Na (soil)/K-Na (plant), a prominent complementary ion effect is indicated. For turnips, these values are virtually constant at all exchange-capacity levels; for oats, they are nearly constant for

TABLE 5  
*Ca-Na and K-Na ratios of soils and of oat and turnip tops*

Ca-Na			K-Na			K-Na (SOIL)/K-Na (PLANT)	
Soil	Oats	Turnips	Soil	Oats	Turnips	Oats	Turnips
<i>Cation-exchange capacity—20.8 m.e.</i>							
19	0.3	2.2	0.13	0.14	0.21	0.9	0.6
19	0.3	4.0	0.23	0.23	0.45	1.0	0.5
19	0.4	7.0	0.48	0.59	1.34	0.8	0.4
19	0.7	10.4	1.50	1.91	4.80	0.8	0.3
<i>Cation-exchange capacity—10.4 m.e.</i>							
9	0.2	2.2	0.08	0.15	0.17	0.5	0.5
9	0.2	2.8	0.14	0.20	0.26	0.7	0.5
9	0.2	4.1	0.21	0.32	0.55	0.7	0.4
9	0.4	4.8	0.61	0.95	1.73	0.6	0.4
<i>Cation-exchange capacity—5.2 m.e.</i>							
4.5	0.2	2.2	0.05	0.18	0.16	0.3	0.3
4.5	0.2	2.2	0.08	0.18	0.19	0.4	0.4
4.5	0.2	2.5	0.13	0.24	0.28	0.5	0.5
4.5	0.2	3.4	0.30	0.62	0.66	0.5	0.5

each exchange-capacity level, but decrease with decreasing cation-exchange capacity.

*Release of cations with small amounts of HCl and NaNO<sub>3</sub>*

In a previous investigation (13) comparisons were made between the proportionate amounts of cations in plants and in HCl extracts. Such information was found to be helpful in explaining a possible mechanism by which mineral elements are mobilized into the growing plant. Similar studies were made in the present investigation, using varying amounts of HCl and also NaNO<sub>3</sub> on soil samples taken before soybeans were planted. The results with 1 m.e. HCl added on the basis of 100 gm. soil are presented in table 6.

The results show a definite interaction between treatment and release. With increasing Mg and K levels in the soil, release of Ca generally decreases and

Mg and K increase. This complementary ion effect is manifest at all cation-exchange-capacity levels. There are differences in relative and total amounts

TABLE 6  
*Release of cations from soil by 1 m.e. HCl at three cation-exchange capacity levels*

TREATMENT	CATIONS IN SOIL			CATIONS RELEASED			f-VALUES	
	Ca	Mg	K	Ca	Mg	K	fMg	fK
	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.		
<i>Cation-exchange capacity—20.8 m.e.</i>								
1	8.3	0.56	0.225	0.97	0.18	0.138	3.0	5.6
2	8.3	0.56	0.410	0.84	0.18	0.199	3.6	5.0
3	8.3	0.56	0.820	0.68	0.13	0.370	3.2	5.8
4	8.3	0.88	0.196	0.86	0.26	0.102	3.1	5.3
5	8.3	0.88	0.396	0.74	0.25	0.188	3.0	5.2
6	8.3	0.88	0.994	0.57	0.18	0.426	2.9	6.3
7	8.3	1.68	0.188	0.72	0.36	0.086	2.4	5.0
8	8.3	1.68	0.412	0.63	0.33	0.178	2.5	5.6
9	8.3	1.68	0.808	0.51	0.30	0.344	2.7	6.5
10	8.3	0.30	0.08	0.93	0.13	0.049	3.5	5.0
<i>Cation-exchange capacity—10.4 m.e.</i>								
11	4.2	0.28	0.113	0.92	0.12	0.104	2.7	4.4
12	4.2	0.28	0.205	0.79	0.14	0.150	2.9	4.1
13	4.2	0.28	0.410	0.68	0.11	0.350	2.7	4.8
14	4.2	0.44	0.098	0.82	0.16	0.077	2.0	4.2
15	4.2	0.44	0.198	0.68	0.18	0.159	2.4	4.7
16	4.2	0.44	0.497	0.67	0.18	0.390	2.4	4.9
17	4.2	0.84	0.094	0.65	0.26	0.065	1.9	4.2
18	4.2	0.84	0.206	0.64	0.25	0.147	1.9	4.5
19	4.2	0.84	0.404	0.56	0.23	0.286	1.9	4.9
20	4.2	0.15	0.040	0.85	0.09	0.031	2.7	3.8
<i>Cation-exchange capacity—5.2 m.e.</i>								
21	2.1	0.14	0.056	0.78	0.10	0.051	2.1	2.6
22	2.1	0.14	0.102	0.75	0.10	0.093	2.1	2.6
23	2.1	0.14	0.205	0.73	0.08	0.165	1.8	2.4
24	2.1	0.22	0.049	0.78	0.12	0.045	1.6	2.6
25	2.1	0.22	0.099	0.70	0.14	0.084	1.8	2.4
26	2.1	0.22	0.248	0.62	0.13	0.270	1.9	3.6
27	2.1	0.42	0.047	0.66	0.24	0.034	1.7	2.2
28	2.1	0.42	0.103	0.71	0.24	0.088	1.6	2.4
29	2.1	0.42	0.202	0.59	0.20	0.172	1.6	2.8
30	2.1	0.08	0.020	0.83	0.06	0.020	1.9	2.3

of cations released. Total release decreases slightly with decreasing cation-exchange capacity.

Comparison of the results of chemical release with the uptake of cations by

soybeans reveals a number of similarities: 1. Increasing the exchangeable K, for any given level of Mg and Ca, increases K and decreases Ca and Mg in the plants and in the HCl extracts; 2. Increasing exchangeable Mg, for any given level of Ca and K, increases Mg and decreases Ca in the plants and in the HCl extracts; 3. For any given level of exchangeable K, the K content of the plants and HCl extract increases. The Ca and Mg content and release decrease with decreasing cation-exchange capacity; 4. Proportionately more K and Mg than Ca are taken up by the plants or released by HCl, this effect being greater at the higher cation-exchange capacity.

These relationships apply in general also to the results with oats and turnips. In the culture of this plant  $\text{NaNO}_3$  was used. The effect of  $\text{NaNO}_3$  on the release of Ca, Mg, and K of the 20.8 m.e. exchange-capacity soil before soybeans

TABLE 7  
Release of cations from soil by HCl and  $\text{NaNO}_3$

SOIL NO.	RELEASE BY 0.2 M.E. HCl					RELEASE BY 1 M.E. $\text{NaNO}_3$					RELEASE BY 0.5 M.E. HCl + 0.5 M.E. $\text{NaNO}_3$				
	Ca	Mg	K	fMg*	fK*	Ca	Mg	K	fMg*	fK*	Ca	Mg	K	fMg*	fK*
	m.e.	m.e.	m.e.			m.e.	m.e.	m.e.			m.e.	m.e.	m.e.		
1	0.17	0.03	0.051	2.8	11.9	0.32	0.05	0.064	2.6	7.8	0.67	0.10	0.054	2.4	3.2
2	0.15	0.03	0.063	3.3	8.8	0.28	0.04	0.090	2.3	6.8	0.58	0.09	0.098	2.6	3.6
3	0.11	0.03	0.144	4.4	13.4	0.20	0.03	0.176	2.3	9.7	0.53	0.10	0.188	3.1	3.8
4	0.14	0.05	0.040	3.7	12.8	0.27	0.07	0.056	2.5	9.2	0.59	0.16	0.062	2.7	4.6
5	0.11	0.04	0.061	3.2	11.3	0.26	0.05	0.090	1.8	7.0	0.49	0.14	0.117	2.6	4.8
6	0.09	0.04	0.165	4.0	13.8	0.14	0.03	0.210	2.0	11.9	0.32	0.10	0.205	2.9	5.2
7	0.12	0.08	0.035	3.1	12.4	0.24	0.08	0.040	1.6	7.0	0.57	0.21	0.048	1.7	3.5
8	0.10	0.07	0.059	3.4	9.8	0.22	0.07	0.080	1.6	7.0	0.56	0.20	0.100	1.7	3.5
9	0.09	0.05	0.114	2.6	12.0	0.16	0.06	0.178	1.7	10.7	0.40	0.18	0.166	2.1	4.0
10	0.19	0.02	0.020	2.7	10.1	0.30	0.03	0.028	2.5	8.9	0.62	0.06	0.032	2.4	5.0

\* The coefficient is obtained by dividing the Ca-Mg or Ca-K ratio of the exchangeable cations of the soil by the Ca-Mg or Ca-K ratio of the extract, and is designated as fMg or fK.

is shown by the results in table 7. Here the release of cations by 1 m.e. of  $\text{NaNO}_3$  is compared with that by 0.2 m.e. HCl and by a mixture of 0.5 m.e. HCl and 0.5 m.e.  $\text{NaNO}_3$ . Dividing the Ca-Mg or Ca-K ratio of the exchangeable cations in the soil by the Ca-Mg or Ca-K ratio in the extract from HCl or  $\text{NaNO}_3$ , gives a coefficient which is designated as fMg or fK (as distinguished from the cMg, value which refers to the Ca-Mg ratio in the soil divided by the Ca-Mg ratio in the plant). The use of the "f values" has been cited previously (13). The f values have been computed for these soils and are listed in table 7. It is seen that 1 m.e.  $\text{NaNO}_3$  released appreciably more Ca but only slightly more Mg and K than 0.2 m.e. HCl. In the presence of HCl, higher release was largely restricted to Ca and Mg. With respect to the proportionate amounts released, a depressing effect due to  $\text{NaNO}_3$  is indicated from the f values. The fMg values, in particular, are lower. A good complementary ion effect is indicated in all



cases. If the release of Ca, Mg, and K is accomplished by an equivalent amount of  $\text{NaNO}_3$  instead of  $\text{HCl}$ ,  $f\text{Mg}$  will be lower and  $f\text{K}$  higher (compare with results in tables 6 and 7). This is so, because  $f\text{Na}$  is greater than  $f\text{Ca}$  and  $f\text{Mg}$  and has about the same value as  $f\text{K}$ . The Na ion suppresses Ca and Mg relatively more than K, resulting in higher  $f\text{K}$  values.

To facilitate comparison between the proportionate amounts of cations released and those found in the plants, the average  $c$  and  $f$  values for each cation-exchange-capacity level are presented in table 8. With decreasing cation-exchange capacity  $f\text{Mg}$  likewise decreases;  $c\text{Mg}$  decreases insignificantly in soybeans, increases in oats, and is without an effect in turnips; the  $f\text{K}$ ,  $c\text{K}$ , and  $c\text{Na}$  values decrease with decreasing cation-exchange capacity, excepting  $c\text{K}$  in oats, which is not affected.

By plotting the percentage of  $\text{Ca} + \text{Mg} + \text{K}$  released against the average  $f\text{Mg}$  and  $f\text{K}$  values, the relationships shown in figure 1 are obtained. Though

TABLE 8  
Average  $c$  and  $f$  values in relation to cation-exchange capacity

CATION- EXCHANGE CAPACITY	SOYBEANS*		OATS†			TURNIPS‡			1 M.E. HCl		1 M.E. $\text{NaNO}_3$		0.5 M.E. HCl + 0.5 M.E. $\text{NaNO}_3$	
	$c\text{Mg}$	$c\text{K}$	$c\text{Mg}$	$c\text{K}$	$c\text{Na}$	$c\text{Mg}$	$c\text{K}$	$c\text{Na}$	$f\text{Mg}$	$f\text{K}$	$f\text{Mg}$	$f\text{K}$	$f\text{Mg}$	$f\text{K}$
m.e.														
20.8	5.7	13.6	17.2	57.1	42.2	3.7	8.2	2.8	3.0	5.5	2.0	8.4	2.4	4.1
10.4	5.4	11.9	18.4	56.6	33.4	3.6	7.6	2.4	2.4	4.6	...	...	...	...
5.2	5.2	9.8	28.1	59.1	23.6	3.8	4.3	1.7	1.9	2.5	...	...	1.8	2.7

\* Second harvest: percentage release, 4, 6, and 8 for the 20.8, 10.4, and 5.2 levels respectively.

† Percentage release, 3, 4, and 5.

‡ Percentage release, 7, 10, and 13.

$f\text{Mg}$  increases slightly and gradually with decreasing release,  $f\text{K}$  rises greatly at a very low percentage release. With increasing release  $f\text{Mg}$  and  $f\text{K}$  have about the same values. Virtually the same trend was observed with Ruston (12) a soil of the 1:1 lattice type, the results of which are reproduced for comparison in figure 1. The principal difference is that the coefficients for the mineral soil are lower than those for the organic soil, the trend being the same.

When the sum of  $\text{Ca} + \text{Mg} + \text{K}$  of the plants is taken and expressed in terms of percentage release, comparisons between the  $f$  and  $c$  values can be made. The percentages of the total cations removed by soybeans, oats and turnip tops for three cation-exchange capacity levels are given as footnotes in table 8. By taking the corresponding  $c$  values, and by inspection with the results in figure 1, it is seen that these values for soybeans and turnips fall in the same range as the  $f$  values found for  $\text{HCl}$  release. The  $c$  values for oats, however, are very much greater. The  $c\text{Mg}$  and  $c\text{K}$  values calculated for cotton (12) at 10 per cent release were 3.2 and 5.3 respectively, which by inspection are seen also to fall in the same range of  $f$  values for a comparable release.



## DISCUSSION

On the basis of the present and previous results (13) the soil properties influencing the total and proportionate amounts of cations in plants are reflected by the amounts of these cations extracted from the soil by small amounts of HCl. This is further evidence that cations in the soil are mobilized into the plant by H ions (1, 2, 3, 6, 18). At the actively absorbing root-soil colloid interphase the H ions may arise from the dissociation of  $\text{CO}_2$ -charged  $\text{H}_2\text{O}$  or excreted organic acids, or they may be dissociated directly from the negatively charged

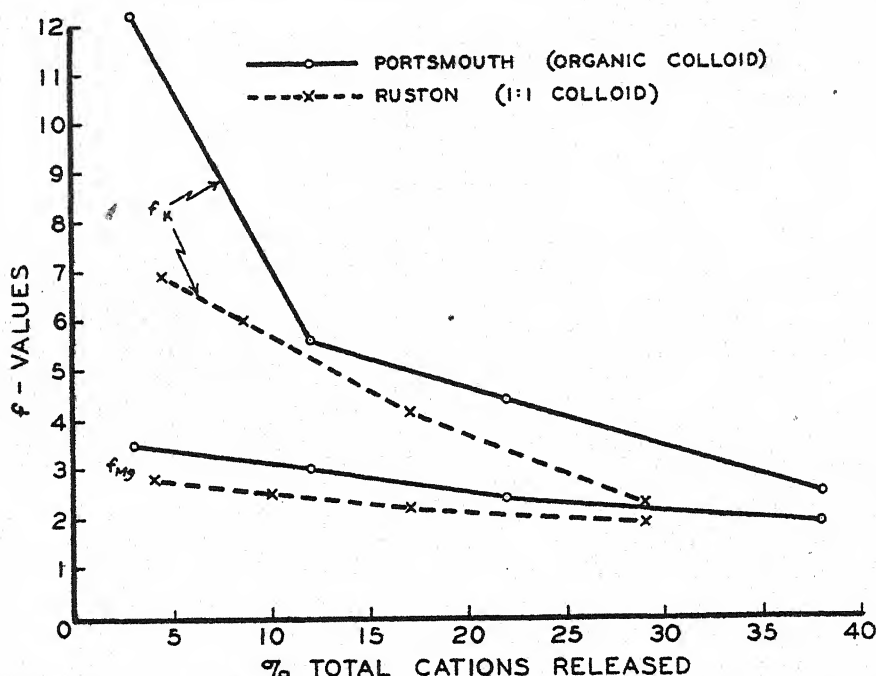


FIG. 1. RELATIONSHIPS BETWEEN PERCENTAGE CATIONS RELEASED AND CORRESPONDING  $f$ -VALUES

root membranes. Roots are known to evolve large quantities of  $\text{CO}_2$ , varying with different plant species (18) and respiration activities (6, 18). The relationship between  $\text{CO}_2$  production of peas and barley and the proportionate amounts of cations taken up by the plants is well illustrated by the results of Newton (16). His data have been converted so as to compare relative  $\text{CO}_2$  production with plant composition, expressed as milliequivalents, and are reproduced in table 9. When grown in the same soil, peas, compared to barley, contained relatively more Ca than Mg or K. When grown in the same solution, the plants contained relatively more Ca than Mg but the difference in cation content between species was small. The plant, it appears, establishes its own cation concentration environment at the colloid-root interphase resulting from its respiratory activity.

The distribution of cations at the soil colloid-root interphase is subject to changes in the same direction whether induced by differences in  $\text{CO}_2$  production between plant species, increased respiration activity of the same plant species, or changes in the cation-exchange capacity at a constant degree of base saturation and with constant cation ratios. Increasing  $\text{CO}_2$  production yields, in effect, a higher concentration of H ions, causing a greater replacement of cations from the colloid. Decreasing the cation-exchange capacity has the same effect, since, for a given root respiration activity, the effective H per unit surface of colloid increases. Since Ca is more strongly adsorbed, the proportion of Ca to the more easily replaceable K in the colloid-root zone will increase with increasing H concentration. The absorption by the plant of relatively more Ca than K,

TABLE 9  
*Relationship between  $\text{CO}_2$  production and mineral composition of  
peas and barley grown in soil and solution culture\**

CROP	CULTURE MEDIUM	RELATIVE $\text{CO}_2$ PRODUCTION	COMPOSITION				
			Ca	Mg	K	Ca-Mg	Ca-K
			<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>		
Peas.....	Soil	100	80	83	151	0.96	0.53
Barley.....	Soil	46	35	58	138	0.60	0.25
Peas.....	Solution	100	60	33	133	1.82	0.45
Barley.....	Solution	46	50	33	125	1.52	0.40

\* After Newton (16).

on lowering the cation-exchange capacity, was observed in the previous experiment with soybeans and cotton (11, 13). In the present study, this was the case with soybeans and turnips but not with oats. A reason for these differences may be offered as follows: From the relative Ca contents of soybeans, cotton, turnips, and oats, it may be implied that the first three are higher producers of  $\text{CO}_2$  than are oats. Under these conditions the colloid-root interphase of turnips, for example, would be dominated by Ca ions to a greater extent than that of oats. It should be recalled that for both crops a constant amount of  $\text{NaNO}_3$  was used. With decreasing cation-exchange capacity, the concentration of the Na ions in relation to the total exchangeable cations was therefore increased. It should be recalled, further, that Na has the effect of suppressing the release of Ca. This effect is greater in the presence of smaller amounts of hydrogen ions. Since the amount of hydrogen ions produced in the case of oats is presumably lower, the release of Ca by the soil in the presence of oats is smaller. Hence, Na will be more effective in suppressing Ca in oats than in turnips where the release of Ca is high. The present experiment as set up does not yield any absolute proof of the correctness of this contention.

Further evidence is found from an examination of data reported by Marshall (10). The presence of Na on the colloid at the same level of Ca, Mg, and K greatly suppressed the Ca in bluegrass but it had little effect on the Ca in sweet

clover and lespedeza. Under these conditions the K was slightly, but inconsistently, increased. This is as would be expected on the basis of the explanation given above; since bluegrass released much less Ca than did lespedeza and sweet clover. The Ca concentrations at the colloid-root interphase may be visualized as lower with bluegrass than with sweet clover and lespedeza; hence the difference in the ability of the Na ions to suppress the concentration of Ca. Differences due to type of colloid or degree of Ca saturation, as they influence Ca mobility or activity, would be expected to be equally as important as differences between plant species. As the Ca activity on the colloid increases, the effect of Na on suppressing the concentration of Ca decreases.

*Complementary ion effects and cation constant equivalency*

It has been suggested that the absorption of cations by plants is increased by treatments which increase their organic acid or protein constituents. Marshall (10) found some relationship between the total sum of cations and the nitrogen in different plant species. Though there are appreciable differences in the total cation contents between plant species and at different stages of growth, the sum of cations has been found to be remarkably constant (5, 7, 8, 9, 10). These observations are confirmed by the results in this investigation. Re-examination of previous results with cotton and soybeans grown on different types of colloids shows this also. In another experiment with cotton (12), as pointed out by Lucas and Scarseth (9) the totals increased with increasing degree of Ca saturation. In this study Na in the plants was not determined. Unfortunately, materials for analysis were no longer available which would permit a check on this point. On the basis of the results with Na in the present investigation this assumption is probably correct, since Na appreciably suppresses the release or uptake of Ca. This would be particularly true at the lower degrees of Ca saturation. It is, however, also conceivable that the complementary ions were  $\text{NH}_4$  or possibly H.

It seems rather certain that the prerequisite for cation equivalent constancy is the complementary ion effect. This effect is great between highly active ions such as K and Na and it is small between less active ions such as Ca and Mg. The effect of substitution of one cation for another depends on the distribution of the cations throughout the growing media. By applying part of the ions in separate root zones the complementary ion effect is diminished, with the result that the total uptake of each respective ion is also increased in the plant (1, 15). This effect is observed in localized placement of fertilizer salts or in additions of ions that are not in a homogeneous solution or that have not assumed the status of exchangeable ions. Under such conditions the ions may act independently of one another at the various root surfaces, and little or no complementary ion effect is evident. Results to this effect are indicated by the data in table 10, computed from previous experimental work where cotton and soybeans were grown on Ruston soil (12). Details of treatments are given as footnotes to table 10.

With the salts mechanically distributed or so located with regard to various



root surfaces that they act independently of one another, the Ca-K ratio in cotton is virtually constant over a wide range of Ca-K ratios in the soil. The  $cK$  coefficient under these conditions increases, therefore, with increasing cation ratios and indicates no complementary effects. With subsequent removal of soluble salts and repeated mixing, adequate distribution was achieved, either because of a greater homogeneity of the soil solution or because the ions are distributed on the colloid particles. The result is a high complementary ion effect.

Many conflicting findings reported in the literature on the effect of one cation upon another are probably explained on the basis of the foregoing results. Soils that have been recently limed or fertilized contain in their various portions many different cation ratios. The analysis of the plant shows merely the average effect. Differences in cation ratios in the soil are also brought about

TABLE 10  
*Cation ratios and  $cK$  values of cotton and soybeans before and after removal of salts by leaching with  $H_2O$*   
Soil used, Ruston fine sandy loam (12)

COTTON BEFORE LEACHING*			COTTON AFTER LEACHING†			SOYBEANS BEFORE LEACHING‡			SOYBEANS AFTER LEACHING§		
Ca-K		$cK$	Ca-K		$cK$	Ca-K		$cK$	Ca-K		$cK$
Soil	Plant		Soil	Plant		Soil	Plant		Soil	Plant	
12.0	1.8	6.8	14.5	3.7	3.9	11.6	2.0	5.8	15.8	3.3	4.8
22.4	1.9	11.7	21.6	4.2	5.1	21.1	3.2	6.6	25.5	4.2	6.1
33.6	2.0	16.8	34.4	8.4	4.1	33.6	4.4	7.6	33.8	5.5	6.1
44.8	2.2	20.3	39.3	8.0	4.9	41.3	5.1	8.1	38.5	6.1	6.3
56.0	2.1	26.7	61.0	13.8	4.4	60.9	4.9	12.4	51.1	6.6	7.7

\*  $Ca(OH)_2$  and  $K_2SO_4$  added in solid form, mechanically mixed and seeded to cotton. \*

† Cotton after soybeans and after leaching with  $H_2O$ . (See previous report (12).)

‡ Soybeans after cotton, no further additions of salts.

§ Soybeans after cotton previously leached with  $H_2O$ .

during the growing period as a result of nutrient losses through leaching and plant removal. If plant roots extend unrestricted into zones having similar cation ratios, little change in the proportionate amounts of cations absorbed during the growing season may be expected. If root extension is restricted, the amounts of cations absorbed during the growing season will vary in proportion to the degree of change taking place in the cation ratios of the soil. The results with soybeans for the first and second harvest may be explained on this basis. These changes will be greater, the larger the  $c$  values, since there would be a greater difference between the ratio of adsorption and the ratios present in the soil. The  $c$  values of soybeans are greater than those of turnips and cotton. Hence, the Ca-Mg and Ca-K ratios for the early and late harvests were about the same in the turnip and cotton crops, whereas they increased somewhat in soybeans. Oats, having very high  $c$  values, should differ even more markedly. Results of this are not available. Extreme  $c$  values were calculated for Kentucky

bluegrass (high  $c$  values) and Korean lespedeza from data reported by Marshall (10). His analysis showed a marked difference in the Ca-K ratio of bluegrass between an early and late cutting, whereas the Ca-K ratios of lespedeza remained virtually the same.

#### *Practical applications*

One objective involving the relationships between soil properties and growth and mineral content of plants has been concerned with the direction in which chemical methods for measuring nutrient requirements should be guided. In humid regions first consideration should be given to determination of that degree of Ca saturation above which plants no longer show any vegetative response. A satisfactory method for determining this point is to add HCl in amounts equivalent to the exchangeable Ca, and then to determine the Ca released after a short period of shaking. This technique was used in the previous experiment with soybeans (13). The release of Ca was found to increase with increasing degree of saturation. For any given degree of saturation the release differed with the type of colloid. The vegetative response of soybeans was likewise different. The results showed no further increase in growth when the release of Ca was about 35 per cent, although the degree of Ca saturation varied from 20 (muck) to 80 (White Store). For Durham and Creedmoor soils these values were 40 and 60 per cent respectively. The values for percentage Ca release should be different with crops having different Ca requirements. The order of these requirements for various crops worked out by Truog (19) may serve as a guide, but the order given did not take into account the effects of soil colloid properties and the effects of other cations. Both are important factors in influencing the uptake of Ca. The effect of other cations can be evaluated from a calculation of the average  $c$  values. It should be recalled that  $cCa = 1$ , whereas  $cMg$ ,  $cK$ , and  $cNa$  are greater than 1, the values varying with different soil conditions and crops. The average  $c$  value will be smaller if the total and proportionate amounts of Ca in the plant are large as compared to the other cations. The mean  $c$  value is calculated from the relationship:

$$cM = \frac{Ca c_{Ca} + Mg c_{Mg} + K c_K + Na c_{Na}}{S \cdot 10}$$

where Ca, Mg, etc. = m.e. cations in the plant,  $cCa$ ,  $cMg$ , etc. =  $c$  values calculated as previously described and  $S$  = sum of cations in the plant (in milliequivalents).

Calculated from the data for soybeans (second harvest), turnips, and oats,  $cM = 0.5$ ,  $0.2$ , and  $3.2$  respectively. The  $cM$  value for cotton was found to be  $0.3$ . The average  $cM$  values were calculated from data reported by Bear *et al.* (5) for the first and the eighth harvests of alfalfa, and were  $0.5$  and  $0.3$  respectively. For alfalfa reported by Lucas *et al.* (8), it was found to be  $0.3$  and for Timothy it was  $9.1$ . Lucas *et al.* also grew red and alsike clover on limed and unlimed soils. When the data from the unlimed soils of Bedford and Clermont were omitted, the  $cM$  values calculated for red and alsike clover



were 0.4 and 0.6 respectively. These crops may thus be arranged in increasing order of Ca needs as follows: timothy, oats, alsike clover, soybeans, red clover, alfalfa, cotton, turnips.

Small grains such as oats are grown on North Carolina soils that are as low as 20 per cent Ca-saturated. The corresponding Ca release is approximately 20 per cent. At the other extreme, alfalfa is grown successfully on soils 60-70 per cent Ca-saturated. The Ca release in this case corresponds to approximately 55-65 per cent. The practical useful range lies, therefore, within these limits. Suppose that 70 per cent Ca release is taken to correspond to the lowest  $cM$  value (0.2 for cotton and turnips) and 20 per cent as the lowest Ca release. If these values were considered together with some of the intermediate values,  $cM$  could be plotted against percentage release. If this were done, a curve would be obtained which begins to flatten out when  $cM$  is greater than 1.4. Hence, whenever  $cM$  is greater than 1.4, a release of approximately 20 per cent would correspond to Ca sufficiency for these crops. With  $cM$  values smaller than 1.4, the percentage release required will increase with decreasing  $cM$ . If these data were plotted as indicated, the required minimum percentage release for some of the crops would be approximately as follows: turnips 70, cotton 60, alfalfa 55, red clover 45, soybeans 35, alsike clover 30, oats and timothy 20.

In determining the Ca released it must be made fairly certain that the source is exchangeable Ca,  $\text{CaCO}_3$ , or  $\text{Ca}(\text{HCO}_3)_2$ . If the Ca release obtained is at the limiting point for a given crop and a significant part of this Ca is due to neutral salts, such as  $\text{CaSO}_4$ , sufficiency may not be indicated. The reason for this is explained on the following basis. In order for the replacement of cations to be effected by the root-derived H, the degree of base saturation must be high enough for this H to be adsorbed by the soil colloid. If at the soil-root interphase, appreciable quantities of neutral salts are present and the degree of base saturation as ascertained from a direct determination of exchangeable H (14) is at the critical limit, the root-derived-H ions may be expected to remain unadsorbed. As such, they make up part of the cationic swarm of ions surrounding the absorbing root surface and add to the competitive ion effect. The presence of soluble salts, furthermore, brings about increased replacement of exchangeable H ions which add to the competitive effects.

#### SUMMARY

A Portsmouth soil, representative of the organic-type colloid, was treated so as to be about 40 per cent saturated with Ca and to contain various levels of Mg and K. Dilutions with sand were made to provide three cation-exchange-capacity levels. In these soils in the greenhouse, soybeans, oats, and turnips were grown. The first crop grown was soybeans, two harvests being taken. This was followed by oats and turnips,  $\text{NaNO}_3$  being used as the source of N. The crops were analyzed for Ca, Mg, K, and Na. In the laboratory, determinations were made of the amounts of these cations that were extracted from the soil by small amounts of HCl (to supply 1.0 m.e. H or less). The principal results were as follows:

1. At all cation-exchange-capacity levels, increasing the concentrations of Mg or K in the soil increased the amounts of these cations extracted by HCl and the amounts taken up by the plants. At the same time, the Ca decreased as a result of increasing K levels. This reciprocal interaction had little effect on the sum of the cations in soybeans, and the sum was decreased only slightly in oats and turnips with increasing levels of K.

2. At a constant Mg or K level in the soil, the Mg and K content in the plant and in the HCl extracts increased with decreasing cation-exchange capacity. At a constant Ca-Mg or Ca-K ratio the reverse was true, notably with respect to K.

3. Increasing the Ca-Mg and Ca-K ratios in the soil increased these ratios in the plants and in the HCl extracts. Increasing the K-Na ratio in the soil increased the K-Na ratio in turnips and oats.

4. A strong complementary ion effect was indicated between K and Na in oats and turnips, and between Ca and K in all plants and in the HCl extracts. A moderate effect was noted in all cases between Ca and Mg. Localized applications of Ca and K salts in the soil resulted in negligible complementary ion effects in plants.

5. The mineral composition of the three plant species differed primarily with respect to their contents of Ca. Oats contained the lowest amounts of Ca; and turnips, the highest.

6. The addition of  $\text{NaNO}_3$  has the effect of replacing exchangeable K relatively more than Ca. This effect is less in the presence of higher concentrations of H ions, which promote the release of Ca. Thus, oats mobilized smaller quantities of Ca into the plant and contained proportionately more K than Ca as a result of increased additions of Na. The ratio of Ca to K in turnips, however, was little influenced by an increase of  $\text{NaNO}_3$  in the soil.

7. The ratios between Mg and Ca or K and Ca in soybeans and turnips was of the same order as their ratios in solution when effected by a very small release through hydrolysis or HCl. This relationship did not hold for oats where the ratios of Mg to Ca or K to Ca were very much greater.

8. It is concluded that by supplementing the determination of the exchangeable cations with measurements of their partial release, soil-plant-nutrient relationships can be more advantageously interpreted. Finally, a scheme has been suggested for evaluating the Ca requirements of different plant species.

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# EFFECTS OF WHEAT STRAW, LESPEDEZA SERICEA HAY, AND FARMYARD MANURE, AS SOIL MULCHES, ON THE CONSERVATION OF MOISTURE AND THE PRODUCTION OF NITRATES

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The use of a straw mulch is an ancient farm practice. King (2, pp. 112, 412) referred to it in 1911 as current in Japan in the cultivation of both orchard and garden crops. Conservation of soil moisture, prevention of erosion, and weed control have long been stressed as the chief effects, but detrimental results have been noted, especially on soils poor in nitrogen.

A number of investigators have found that a straw mulch materially reduces the formation of nitrates. This was shown conclusively in field trials at the Kansas Experiment Station, by Scott (3), who found that of all the experimental treatments, wheat straw applied as a top-dressing at the rate of 4 tons per acre resulted in the highest soil moisture, the lowest temperature, and the lowest nitrate content of the soil throughout the summer season. At the Missouri Station, Albrect and Uhland (1) found that a heavy straw mulch of 6 tons per acre caused a depression in nitrate accumulation. They reported, "Facts all indicate that the straw mulch in applications as heavy as 6 tons per acre, cuts down evaporation, thereby increasing the moisture, lowering the temperature, and preventing the normal exchange of air, all of which induces a poor physical condition and unfavorable environment for nitrate accumulation." Recently, Turk and Partridge (4), at the Michigan Station, published the results of experiments on the effects of various mulching materials, using lysimeters, which admit of specially valuable quantitative data. They found that "The effectiveness of an artificial mulch varies greatly with the type of soil, kind of mulch and climatic conditions."

The present paper deals with results obtained with uncropped lysimeters containing two types of Tennessee soil and the use of three kinds of mulch materials—wheat straw, legume hay from *Lespedeza sericea*, and farmyard manure.

## PRELIMINARY PROCEDURE

Fifty-six lysimeter tanks were used, each 12 inches deep and 1/10,000 acre in surface area. Each tank was thoroughly washed and painted with asphalt before soil placement. Containers for the percolates also were cleaned and painted with asphalt.

Two soil types were used, Cumberland loam from the University Farm and Calhoun silt loam from the West Tennessee Station. The two soils were of very different character. The Cumberland was brown-colored and very similar to Decatur silt loam. The clay content was nearly 19 per cent and the silt content 48 per cent. This soil was of excellent texture and structure, of good



internal drainage, and well adapted to the production of general farm and garden crops. The Calhoun soil had a clay content of only 9 per cent and a high content of silt, 79 per cent. The internal drainage was poor. It is a type of gray-colored soil rated as inferior for most cultivated crops but much used for lespedeza pasture. Both soils had been used in the same tanks in a long-continued project which greatly reduced their supply of available nitrogen. Each soil was taken up according to limed and unlimed treatments (14 of each). Within this treatment the soils were thoroughly mixed and screened before replacement, which was at the rate of 195 pounds per tank on air-dry basis. The first tanks were taken up August 17, 1942, and the last soil returned August 27, 1942.

Before replacement of the soil, 20 pounds of damp, coarse sand (recovered by washing) was tamped into the bottom of each tank. Then 100 pounds of soil was carefully weighed and tamped into each tank. The fertilizer materials were added and thoroughly mixed with the remaining 95 pounds. The soil was about 6 inches deep when settled.

TABLE 1  
*Analyses of mulch materials, on air-dry basis, as applied*

LOT NO.	MATERIAL	MOISTURE	N	TOTAL ASH
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
6849	Wheat straw	10.0	0.38	5.40
6850	Sericea hay	10.0	1.98	3.45
6851	Manure	12.7	2.26	20.63

The fertilizer materials incorporated in the soil and the tanks to which they were applied are given below:

FERTILIZER MATERIALS	RATE OF APPLICATION, POUNDS PER ACRE	TANKS RECEIVING THE APPLICATION
Superphosphate, 16 per cent. ....	600	1-28
Muriate of potash. ....	100	1-28
Manure. ....	10,000	4, 5, 6, 7, 11, 12, 13, 14, 18, 19, 20; 21, 25, 26, 27, 28

Chemical analyses of the various mulch materials are given in table 1. The mulches, chopped to lengths of approximately  $\frac{1}{4}$  to 1 inch, were applied at the rate of 5 tons of air-dry matter per acre.

The nitrogen content per 5 tons was as follows:

Wheat straw .....	38 pounds
Sericea hay .....	198 pounds
Manure .....	226 pounds

The experimental treatments were as follows:



TREATMENT	LYSIMETER NUMBERS OF EACH SOIL SERIES	
	Limed	Unlimed
Check (no mulch).....	1, 15	8, 22
Sericea hay.....	2, 16	9, 23
Wheat straw.....	3, 17	10, 24
Sericea hay + incorporated manure.....	4, 18	11, 25
Wheat straw + incorporated manure.....	5, 19	12, 26
Manure.....	6, 20	13, 27
No mulch + incorporated manure.....	7, 21	14, 28

The tanks were kept covered until all treatments were completed. To hold the mulch in place and prevent loss, a coarse wire screen was placed on top of each application. One-half acre-inch of water (11.32 pounds) was applied September 6, 1942, by means of a sprinkling can. An additional  $\frac{1}{2}$  acre-inch of water was applied similarly September 7, 1942. No watering was done afterward.

## RESULTS

### *Effects of liming*

Data from the limed and unlimed tanks showed no positive differences with regard to either moisture losses or nitrate production; hence further discussion of the subject has been omitted.

### *Moisture losses*

The effect of a mulch is to retard the loss of soil moisture by evaporation and to increase loss by leaching. Table 2 shows the summarized data for each of the 3 years. As would be expected, all mulch materials were most effective in saving moisture the first year. In Cumberland loam, wheat straw reduced the loss by evaporation from 42.3 per cent of the total rainfall, as occurred in the unmulched series 1 and 7, to only 12.4 per cent, series 3 and 5. Similarly, the evaporation loss of 40.9 per cent of the rainfall from the unmulched Calhoun silt loam was reduced by the straw mulch to only 16.0 per cent. The sericea hay mulch, series 2 and 3, which contained, as applied, 2 per cent more organic matter than the wheat straw, allowed an evaporation loss of 30.5 per cent for Cumberland loam and 25.2 per cent for Calhoun silt loam. This reduction in efficiency as compared with wheat straw is attributed chiefly to the more rapid decomposition of the sericea hay. The manure mulch, which contained very little straw, was the least effective, the evaporation losses for series 6 being 36.0 per cent for Cumberland loam and 34.8 per cent for Calhoun silt loam. The manure contained about 15 per cent less organic matter than the wheat straw and disappeared even more rapidly than the sericea hay. In fact, its effectiveness in preventing evaporation after the first year was not clearly in evidence.

TABLE 2  
Percolates from lysimeter tanks for 3-year period  
Average of four tanks for each series

SERIES	TREATMENT	PERCOLATES		
		1st year	2nd year	3rd year
		kgm.	kgm.	kgm.
<i>Cumberland loam</i>				
1	None.....	286.0	231.6	334.8
2	Sericea mulch.....	347.9	257.3	344.2
3	Wheat-straw mulch.....	431.8	279.9	340.1
4	Sericea mulch, manure incorporated.....	342.9	254.8	340.6
5	Wheat-straw mulch, manure incorporated..	438.8	289.1	346.8
6	Manure mulch.....	318.3	238.2	337.2
7	Manure incorporated.....	287.2	233.7	339.2
	Rainfall per tank.....	496.8	424.2	523.2
<i>Calhoun silt loam</i>				
1	None.....	293.4	237.2	341.4
2	Sericea mulch.....	363.3	251.4	348.3
3	Wheat-straw mulch.....	414.3	285.7	367.7
4	Sericea mulch, manure incorporated.....	380.5	262.6	349.4
5	Wheat-straw mulch, manure incorporated..	420.2	280.9	369.0
6	Manure mulch.....	323.8	238.8	342.5
7	Manure incorporated.....	293.5	237.3	344.4
	Rainfall per tank.....	496.8	424.2	523.2

The data of table 2 are summarized, in condensed form, as follows (100 per cent effectiveness would mean no loss of soil moisture by evaporation):

MULCH		CUMBERLAND LOAM, EFFECTIVENESS	CALHOUN SILT LOAM, EFFECTIVENESS
		<i>per cent</i>	<i>per cent</i>
1st year	{ Straw.....	70.7	60.9
	{ Sericea.....	27.9	38.4
	{ Manure.....	14.9	14.9
2nd year	{ Straw.....	27.2	24.7
	{ Sericea.....	12.4	10.7
	{ Manure.....	3.1	0.1
3rd year	{ Straw.....	0.3	1.5
	{ Sericea.....	0.3	0.2
	{ Manure.....	0.0	0.0

Though greatly reduced in effectiveness, the straw mulch continued to be decidedly superior to sericea the second year, but neither was of moment the third year.

*Nitrate nitrogen in percolates*

Table 3 summarizes, in pounds per acre, the nitrate nitrogen found in the percolates of each of the seven series. In every case, the amount is the average of four replications. The percentage recovery of the nitrogen applied in the several treatments is given in table 4.

TABLE 3

*Nitrate nitrogen in percolates from lysimeter tanks*  
Average, in pounds per acre, of four tanks for each series

SERIES	TREATMENT	NITRATE NITROGEN PERCOLATES							
		Cumberland loam				Calhoun silt loam			
		1st year	2nd year	3rd year	Total	1st year	2nd year	3rd year	Total
1	No treatment.....	41.3	27.4	13.0	81.7	34.6	25.4	14.4	74.4
2	Sericea mulch.....	95.5	41.9	35.7	173.1	84.9	49.0	21.8	155.7
3	Wheat-straw mulch.....	21.0	18.4	17.4	56.8	11.8	19.7	16.4	47.9
4	Sericea mulch, manure incorporated.....	139.7	66.5	54.6	260.8	89.5	68.2	42.3	200.0
5	Wheat-straw mulch, manure incorporated.....	60.4	35.0	35.3	130.7	33.4	28.4	26.3	88.1
6	Manure mulch.....	102.0	44.7	26.1	172.8	90.4	40.4	22.7	153.5
7	Manure incorporated.....	101.6	49.9	26.4	177.9	80.9	48.6	26.1	155.6

TABLE 4

*Calculated recovery from lysimeter tanks of applied nitrogen per acre*

SERIES	TREATMENT	NITROGEN IN TREATMENT lbs.	RECOVERY OF APPLIED NITROGEN							
			Cumberland loam				Calhoun silt loam			
			1st year	2nd year	3rd year	Total 3 years	1st year	2nd year	3rd year	Total 3 years
			per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
2	Sericea mulch.....	198	23.37	7.32	11.46	46.15	25.40	11.92	3.74	41.06
3	Wheat-straw mulch....	38	(-48.74)*	(-23.70)*	11.58	(-30.48)*	(-63.90)*	(-22.44)*	5.26	(-35.62)*
4	Sericea mulch, manure incorporated.....	424	23.21	9.22	9.81	42.24	12.95	10.09	6.58	29.62
	Wheat-straw mulch, manure incorporated.	264	7.24	2.88	8.45	18.57	(-0.35)*	1.14	4.51	5.64
6	Manure mulch.....	226	26.86	7.65	5.80	40.31	24.69	6.64	3.67	35.00
7	manure incorporated..	226	26.68	9.96	5.93	42.57	20.49	10.26	5.18	35.93

\* Percentage below no treatment.

For the 3-year period, the calculated recovery of the nitrogen in the sericea mulch of series 2 was 46.15 per cent for Cumberland loam and 41.06 per cent for Calhoun silt loam. It is of interest that 59.3 per cent of the total was obtained the first year in the Cumberland and 62.6 per cent in the Calhoun soil.

Where sericea mulch was used with manure incorporated—series 4—the

nitrogen recovery in the Cumberland soil was only 4.5 per cent less for the 3-year period than the sum of the calculated recoveries from the sericea mulch of series 2 and the incorporated manure of series 7. By a similar calculation for the Calhoun soil, the nitrogen in the percolates of series 4 was 22.7 per cent less than the sum of the individual recoveries of series 2 and 7. This relatively wide difference in the behavior of the two soils may well be attributed to the poor internal drainage of the Calhoun soil, which often became waterlogged in continued or very heavy rainy weather, a condition unfavorable to the soil organisms on which oxidation processes depend.

In this connection it may be noted that for the 3-year period all nitrogen recoveries were less for the Calhoun than for the Cumberland soil, but the differences were specially marked only in series 4 and 5, the latter where wheat-straw mulch was used with manure incorporated.

A total of 40.31 per cent of the nitrogen in the manure-mulched soils was obtained in the percolates from Cumberland loam and 35.00 per cent in the percolates from the Calhoun soil. Of these amounts, the percentage obtained the first year from the Cumberland soil was 66.63, and from the Calhoun, 79.11. It is of special interest that for both soil types the agreement was close between the recoveries of nitrogen in series 6, where the manure was applied as a mulch, and in series 7, where the manure was incorporated with the soil. In fact, they can be said to be the same within the limits of error for work of this kind.

For both soils, wheat-straw mulch of series 3 resulted in a severe depression of nitrate production. The recovery of nitrate nitrogen in the percolates for the 3-year period was 30.48 per cent below that of the unmulched Cumberland soil, and 35.62 per cent below that of the unmulched Calhoun. For each soil the major loss occurred the first year, amounting to 48.74 per cent below that of the unmulched soil of series 1 for Cumberland loam and 63.9 per cent for the Calhoun soil. The second year the losses were 23.70 and 22.44 per cent respectively. The third year showed a small nitrogen increase over the unmulched tanks of both soil types.

In series 5 where wheat-straw mulch was applied to tanks receiving manure incorporated with the soil, the total nitrogen found in the percolates of Cumberland loam for the 3-year period was 130.7 pounds per acre, or 26.53 per cent less than that obtained from the manured, unmulched tanks of series 7, which yielded 177.9 pounds. Similarly, series 5 of Calhoun silt loam yielded 88.1 pounds of nitrogen, as compared with 155.6 pounds from series 7, a reduction of 43.38 per cent.

Numerous tests of the percolates showed only traces of either nitrites or ammonium salts.

#### DISCUSSION

The depression in nitrate production brought about by a straw mulch has given rise to various hypotheses as to the causative factor or factors. That an organic mulch excludes air and brings about a deficiency of soil oxygen is rather generally assumed to be the prime cause. This explanation, however, is in-



consistent with the experimental data. In series 1 of the Cumberland loam, the no-treatment tanks produced in the 3-year period a total of 81.7 pounds of nitrate nitrogen per acre, but series 3, with the straw mulch, produced only 56.8 pounds. If soil oxygen were the limiting factor, it would be a question how series 5 with a straw mulch could yield 130.7 pounds of nitrate nitrogen.

In an attempt to answer this question, the authors found some of the experimental results with Hillsdale sandy loam presented by Turk and Partridge (4) to be very pertinent. Within the limits of error for lysimeter work, those workers found, as shown in table 5, that a gravel mulch was as effective in preventing loss of moisture by evaporation as either a straw or a stover mulch, and that the nitrate nitrogen obtained in the percolates from the gravel mulch was 89.2 per cent as great as that obtained from the no-mulch lysimeters. It should be noted, however, that their no-mulch lysimeters were "cultivated frequently to maintain a 2-3-inch soil mulch." This means that of the 7-inch soil depth, 30 to 40 per cent was kept well aerated by stirring so that stimulation of nitrate

TABLE 5  
*Total percolate and nitrate nitrogen obtained under each of various  
mulch conditions with Hillsdale soil in a 4-year period*

From Turk and Partridge (4)

MULCH	PERCOLATE	NITROGEN
	<i>pounds</i>	<i>gm.</i>
No mulch.....	4274	70.4
Straw mulch.....	7148	36.7
Stover mulch.....	7085	30.3
Sawdust mulch.....	6694	46.8
Gravel mulch.....	6940	62.8

production was at least possible. The conclusion can hardly be avoided, therefore, that the mulch *per se* is not the prime causative factor in the depression of nitrate production, and the hypothesis is advanced that organic mulches like straw and stover are the source of soluble organic compounds which are the prime cause of lowered production of nitrate nitrogen.

This supposition does not eliminate the air supply as a secondary factor, for the higher content of water in the straw-mulched soil must reduce the air supply and might thereby limit the oxidation capacity to an appreciable degree. In fact, this assumption offers an explanation of the variations in nitrate production between the two soils. Table 4 shows that in series 2, 3, 6, and 7 the percentage recovery of applied nitrogen for the 3-year period was 12 to 17 per cent higher for Cumberland loam than for Calhoun silt loam, but that in series 4, where the nitrogen in the treatments was almost doubled, the recovery was nearly 43 per cent greater for the Cumberland than for the Calhoun soil. Also in series 5, which received straw mulch and manure incorporated, the nitrogen recovery, though very low for both soils, was more than three times as much for the Cumberland as for the Calhoun soil. In short, the Calhoun soil, with its poor internal



drainage, had an appreciably lower oxidation capacity than the Cumberland soil, with its excellent internal drainage, and the differential effect was accentuated under extreme conditions.

#### SUMMARY

The effects of wheat-straw, sericea-hay, and farmyard-manure mulches on evaporation losses and nitrate production during a 3-year period were studied on Cumberland loam and Calhoun silt loam in 56 lysimeter tanks 12 inches deep and of 1/10,000 acre area. All trials were replicated four times for each soil. No crops were grown, and the soils were left undisturbed, except that weeds were pulled when small.

The straw mulch proved far superior to the others in preventing loss of soil moisture by evaporation. The first year's losses for Cumberland loam were reduced from 42.3 per cent of the total rainfall for the unmulched tanks to 12.4 per cent for the straw-mulched tanks, 30.5 per cent for the sericea hay, and 36 per cent for the manure, each applied at the rate of 5 tons per acre of air-dry substance. The corresponding losses for the Calhoun soil were 40.9 per cent for the unmulched tanks, 16 per cent for the straw-mulched, 25.2 per cent for the sericea-mulched, and 34.8 per cent for the manure-mulched.

The effectiveness of all the mulches was greatly reduced the second year. In particular, the manure mulch, which contained wood shavings but very little straw, was effective only the first year.

The mulch effects of both the straw and the sericea were barely in evidence the third year.

The straw mulch greatly reduced the production of nitrates in both soils. In the 3-year period, 81.7 pounds of nitrogen per acre was obtained from the no-treatment tanks of Cumberland loam, but only 56.8 pounds from the straw-mulched; and for the Calhoun soil, only 47.9 pounds, as compared with 74.4 pounds for the no-treatment tanks.

The total nitrate nitrogen for the 3-year period obtained from the manure-incorporation tanks of the Cumberland soil was 177.9 pounds, but the straw mulch reduced it to 130.7 pounds. In like manner, in the Calhoun soil the reduction was from 155.6 pounds to 88.1 pounds.

With the sericea-hay mulch, the total nitrate nitrogen in the percolates of the 3-year period was 173.1 pounds for the Cumberland soil and 155.7 pounds for the Calhoun.

With manure incorporated, the sericea mulch increased the recovery to 260.8 pounds for the Cumberland soil and to 200.0 pounds for the Calhoun.

The nitrate nitrogen obtained from the manure-mulched tanks of each kind of soil was only slightly under that from the manure-incorporated tanks for each of the 3 years. In fact, the differences were the same within the limits of error for work of this kind.

The sericea mulch showed a total recovery of 46.15 per cent of the nitrogen applied to the Cumberland soil and 41.06 per cent in the case of the Calhoun soil.

Of the nitrogen in the incorporated manure, 42.57 per cent was recovered in the percolates of the Cumberland soil and 35.93 per cent in those of the Calhoun soil.

The straw-mulch effect in depressing nitrate production was attributed primarily not to exclusion of the soil air supply, but to soluble derivatives leached into the soil. Corroborative evidence cited showed that a gravel mulch on Hillsdale sandy loam can equal a straw mulch in preventing loss of soil moisture by evaporation, but with minor lowering of nitrate production.

Although the two soil types were widely different in both texture and structure, the results obtained were similar in general character.

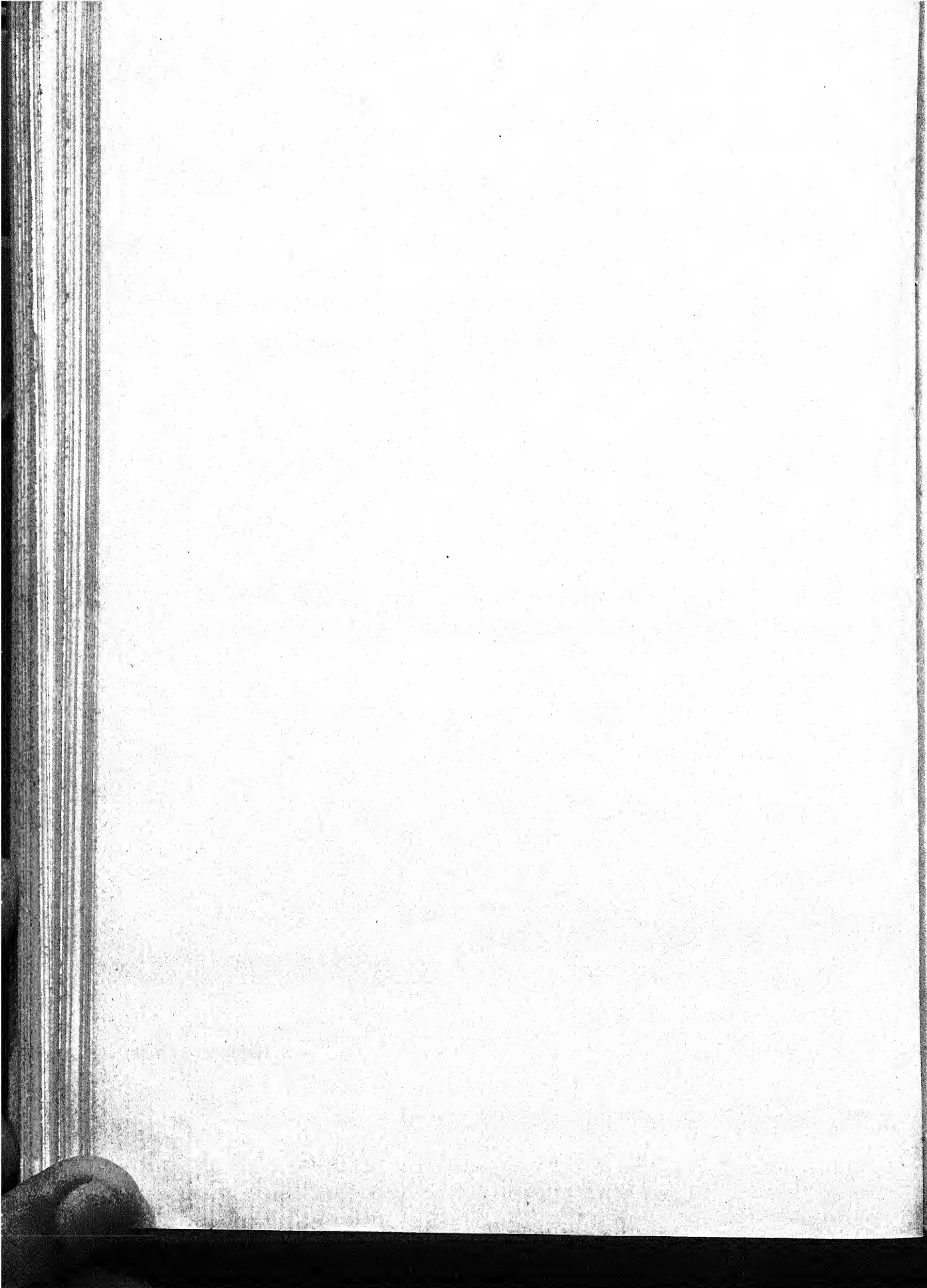
The quantity of percolate for each soil was nearly the same under all conditions.

The nitrogen found in the percolates for the 3-year period was less for Calhoun silt loam than for Cumberland loam under all experimental conditions and of like order in five of the seven series.

Under comparatively extreme conditions—series 4 and 5—the Cumberland soil far surpassed the Calhoun in nitrate production. This was attributed to the more limited air supply of the Calhoun soil because of its poor internal drainage.

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# THE PRESENCE AND DETERMINATION OF MOLYBDENUM AND RARE EARTHS IN PHOSPHATE ROCK

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Recent work in Southwestern Australia shows that the application of as little as  $\frac{1}{8}$  ounce of molybdenum per acre is economically useful for the growth of subterranean clover (1). Steinberg (12) and Arnon and Stout (2) have reported molybdenum essential for plant growth.

The extreme complexity of composition of phosphate rock has long been known (8). It is common knowledge that application of superphosphate has beneficial effects in many instances where the plant does not respond to phosphorus. This is not due to the gypsum contained in the superphosphate. It is a natural conclusion that some minor elements in the complex superphosphate may be responsible. In this study, phosphate rocks from some of the more important sources have been examined for molybdenum. Since this determination leaves a residue in which it is convenient to determine the rare earths, these elements have also been determined. The rare earth elements are taken as an analytical group made up of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, holmium, erbium, thulium, ytterbium, and lutecium. According to Hillebrand (6), these elements are left in the residues when sodium carbonate fusions of rock powders are disintegrated and leached with water.

## REVIEW OF LITERATURE

Jacob *et al.* (8) reported that samples of Florida land pebble, Tennessee blue rock, and Idaho phosphate rock were tested for molybdenum with negative results. They attempted to precipitate extremely small amounts of molybdenum as sulfide. This is especially difficult with such a complex material as phosphate rock. Later the presence of molybdenum in phosphate rock was shown spectrographically by Scribner [see Hoffman and Lundell (7)]. By chemical analysis, Hoffman and Lundell (7) found 2 p.p.m. of  $\text{MoO}_3$  in Bureau of Standards standard sample 56A and 20 p.p.m. in their standard sample 120. Oertel and Stace (9), by spectrographic analysis, found molybdenum present "in parts per million" in phosphate rocks from Algeria, Egypt, and Florida. They did not find molybdenum in Nauru or Ocean Island phosphate rocks.

Starnkevitch-Borneman (11) reported rare earths present in five Russian phosphate rocks in quantities ranging from traces to 0.3 per cent. Hill *et al.* (5) found 0.01 to 0.03 per cent rare earths in colloidal material extracted from

<sup>1</sup> The samples used were prepared and furnished by W. L. Hill. F. S. Grimaldi of the Geological Survey gave advice on the cupferron separation for molybdenum used to check the method given.



Florida soft and Tennessee brown phosphate rock. According to Drobkov (4), the Khibiny apatites, which are an important source of phosphatic fertilizer, contain 0.7 to 3.5 per cent rare earths, and phosphorites contain 0.05 to 0.8 per cent of these elements. Drobkov reported that small amounts of rare earth oxides greatly increased the growth of peas.

#### ANALYTICAL METHODS

Molybdenum is determined by the well-known thiocyanate colorimetric method. The small quantity of silica, however, must first be removed by evaporation and filtration, otherwise an emulsion may form when the solution is extracted with isopropyl ether. This compound is used in place of ethyl ether because it is much less volatile. Rhenium gives the same color as molybdenum under the same conditions. The results given here would include rhenium if present, but there is little probability of enough rhenium being present to affect the results (10).

#### *Solutions required*

1. Standard solution of ammonium molybdate. Dissolve 1.149 gm. ammonium molybdate in 1 liter water stabilized with 2 to 3 ml. strong ammonia. Determine the exact strength by a gravimetric determination of molybdenum as lead molybdate. Then dilute this stronger solution appropriately so that the final solution will contain 0.05 mgm.  $\text{MoO}_3$  per milliliter.
2. Sodium carbonate solution—5 per cent.
3. Five per cent potassium thiocyanate solution.
4. Ten per cent stannous chloride solution in 1:9 HCl.
5. Isopropyl ether.

#### *Fusion*

Weigh out 5 gm. of the finely ground phosphate rock. Mix it intimately with 15 gm.  $\text{Na}_2\text{CO}_3$ . A large platinum crucible is needed to hold the fusion—35 gm. (approximately 30 ml.) or more. The fusion is facilitated by first covering the bottom of the crucible with 0.1 to 0.2 gm. sodium carbonate, then putting in the fusion mixture. Heat the uncovered crucible and contents for 15 minutes over a burner of the Meker type so as to burn off the organic matter in an oxidizing atmosphere and also avoid the possibility of loss of the molybdenum. At this stage there should be only incipient fusion. After this preliminary heating, cover the crucible and increase the temperature gradually to fusion but in such a manner as to avoid loss. Increase the heat to about  $1050^\circ\text{C}$ ., and every 5 minutes remove the cover and swirl the contents of the crucible vigorously. When the fusion becomes quiet, generally in 20 minutes, remove the crucible from the flame and swirl and turn the crucible so that the melt solidifies largely on the sides. Cool the crucible and contents by rolling on a cool slab of alberene or iron. The cake should detach easily from the crucible when inverted over a 250-ml. beaker and rolled gently between the thumb and fingers pressed against the sides.



### *Extraction*

Half fill with water the beaker containing the broken cake, cover and place on a steam bath for 2 or more hours, breaking up the pieces of cake with the stirring rod as the softening process takes place. When the pieces of cake have softened and have been broken into fairly small pieces, pour the liquid into another beaker, transfer the solid matter to a porcelain dish or small mortar, and grind the softened pieces of cake to a fine slurry. Rinse the slurry back into the first beaker with the contents of the second, and finish the transfer by washing. Put the beaker on a steam bath for 15 minutes with occasional stirring, and filter and wash the contents into a large platinum dish. Acidify the filtrate with a moderate excess of HCl. Evaporate to dryness and take up with 7.5 ml. concentrated HCl and water. Filter off the precipitated silica and wash till the volume of the filtrate is about 120 ml.

### *Color development*

Transfer the filtrate to a 200-ml. separatory funnel. The volume should now be about 140 ml. Add 5 ml. of the KCNS solution. Shake, add 5 ml. stannous chloride solution, and shake. After half a minute add 10 ml. isopropyl ether, shake vigorously at least  $\frac{1}{2}$  minute. Allow to stand till the ether layer is clear. A yellow to brown coloration shows the presence of molybdenum. Draw off the water layer and transfer the ether layer to a 25-ml. measuring flask. Rinse with a little ether and extract the solution again with 10 ml. ether, and add this to the first extract. Make the contents of the measuring flask up to volume and compare with a standard prepared as follows:

Measure 125 ml. of the 5 per cent  $\text{Na}_2\text{CO}_3$  solution into a 200-ml. separatory funnel. Add from 0.1 to 10 ml. of the standard molybdate solution or steps of these concentrations. Add 25 ml. concentrated HCl with swirling to release  $\text{CO}_2$ . Cool under a stream of tap water. Then develop the color as above, and compare immediately in a colorimeter, for after separation, the color fades rather rapidly.

When a number of determinations are to be made it will be found quite satisfactory to make the color comparison by looking through the ether layer in the separatory funnel, without any separation. For this comparison a cylindrical separatory funnel is desirable. If a pear-shaped funnel is used, care should be taken to have the ether layer in the same positions in the funnel. When no separation is made, the color seems to be permanent (2 weeks). The color may be matched by a system of titration and shaking when the standard is lower than the determination. In the latter case the shaking should be thorough after each increment.

According to Hillebrand (6), the leached residue from the molybdenum extraction should contain the rare earths. The residues from two molybdenum determinations, representing 10 gm. phosphate rock, were combined, dissolved in nitric acid, and evaporated. The silica was filtered, washed, decomposed with  $\text{HF} + \text{HNO}_3$ , and the residues were added to the main filtrate. In part of the determinations the phosphorus was precipitated as phosphomolybdate. This

was a long and tedious process because of the relatively huge quantities of molybdate required and the delayed and incomplete precipitation of the phosphomolybdate. This is presumably due to the presence of fluorides. The phosphomolybdate was worked over for rare earths by separation in strong ammonia. The separation of calcium and phosphorus was much easier by Reynosos' method (3, p. 497).

In applying Reynosos' method, the solution containing the rare earths was obtained in a volume of about 175 ml. of stronger than 1.1  $\text{HNO}_3$  in a 400-ml. beaker. To this, on the steam bath, 10 gm. mossy tin was added, the beaker covered, and the reaction allowed to proceed for about 2 hours. The tin-phosphorus compound was filtered off and the rare earths were determined in the solution by two precipitations with ammonia, two precipitations with oxalic acid in very small volumes, and an intervening precipitation with ammonia. The residue was treated with an excess of  $\text{KOH}$  and the precipitate examined for rare earths. No rare earths could be detected with certainty in this precipitate. The rare earth determinations of the two methods agreed fairly well. They are probably somewhat low, because of solubility losses. Up to the present, recoveries of known amounts of rare earths added to plant ash have never exceeded 90 per cent in this laboratory.

#### RESULTS

The results obtained for  $\text{MoO}_3$  and rare earths ( $\text{R}_2\text{O}_3$ ) were as follows:

	RARE EARTHS	
	$\text{MoO}_3$	$\text{R}_2\text{O}_3$
	<i>p.p.m.</i>	<i>p.p.m.</i>
Bureau of Standards #56A Tennessee brown rock...	2	150
#909 Tennessee brown rock.....	2	
#2529 Tennessee brown rock.....	1, 2	
Bureau of Standards #120 Florida land pebble....	29	
#910 Florida land pebble.....	31	460
#2521 Florida land pebble.....	26	
#932 Florida hard rock.....	5	140
#1934 Florida land pebble, commercially ground..	98	
#930 Tennessee blue rock.....	5	450
#2280 Tennessee brown rock superphosphate.....	1, 2	
#2530 Tennessee brown rock superphosphate.....	1, 2	
#2532 Florida land pebble superphosphate.....	12	
#773 Idaho phosphate rock.....	49	560
#1232 Montana phosphate rock.....	18	1550
#948 Wyoming phosphate rock*	208	980
#1571 French Morocco phosphate rock.....	9	
#1547 Egyptian phosphate rock.....	62	640
#1551 Tunis phosphate rock*	20	1100
#1567 Naru Island phosphate rock.....	2	110
#2528a Curacao Island phosphate rock.....	1	50

\* These samples contained enough gold to give the purple of Cassius' test in the first precipitation of rare earths by oxalic acid.

*Remarks.* When separated, the ether solution fades after several hours, particularly with low molybdenum contents. This necessitates reading the color rather promptly. In spite of the fact that this does not have the nicety of precision, it is probably more nearly accurate to compare the colors in the separatory funnel, matching the color with titration or having a number of standards than to separate the ether layer and compare in a colorimeter.

The separated silica does not appear to contain any determinable quantity of molybdenum. Likewise, the leached residue does not appear to contain any molybdenum.

The residue of 5 gm. of the commercially ground Florida phosphate rock after fusion with sodium carbonate and extraction with water was dried and fused with 5 gm. of sodium carbonate, and the extract analyzed for molybdenum. There was less than 1 p.p.m.  $\text{MoO}_3$  present in the residue. It was concluded, therefore, that one fusion and extraction was sufficient.

The molybdenum compound with cupferron in relatively strong solutions of hydrochloric acid may be extracted with ethyl nitrate, the extract evaporated, the residue fused with sodium carbonate, and the molybdenum estimated in the extract of this fusion. This method checks satisfactorily with the method given above.

There is considerable loss of platinum from the crucible during the fusion, and in the fusion of some samples, particularly the Idaho phosphate rock, the attack was relatively severe. This sample contained a large amount of organic matter. In one series of analyses the organic matter was burned out of this Idaho sample by putting it in a cold furnace in a porcelain dish and raising to redness. Apparently no molybdenum was lost by this process. The 35-gm. crucibles lose up to 15 mgm. of weight during one fusion and polishing with sea sand.

*Recoveries.* An amount of standard molybdate equivalent to 20 p.p.m. was added to two samples before the fusion. The recoveries were as follows:

	$\text{MoO}_3$ PRESENT	$\text{MoO}_3$ ADDED	$\text{MoO}_3$ RECOVERED	ERROR
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Bureau Standards sample #56A.....	{ 2	20	22.4	+0.4
	{ 2	20	23.0	+1.0
Bureau Standards sample #120.....	{ 29	20	50.0	+1.0
	{ 29	20	49.5	+ .5

#### SUMMARY AND CONCLUSIONS

A method for the combined determinations of molybdenum and rare earths in phosphate rock is outlined. Molybdenum was determined in 20 samples and the rare earths in 11 samples of phosphate rock from different parts of the world. The results indicate that:

1. Tennessee and Island phosphate rocks are relatively low in molybdenum. Florida phosphate rocks and North African phosphate rocks are considerably



higher, generally more than 20 p.p.m. Some western phosphate rocks are very high in molybdenum.

2. Superphosphate retains the molybdenum originally in the phosphate rock.

3. Rare earths are present in phosphate rocks in quantities ranging from 110 to 1550 p.p.m.  $R_2O_3$  in the samples examined.

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# POTASSIUM-SUPPLYING POWER OF VIRGIN AND CROPPED SOILS<sup>1</sup>

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The exchangeable form of potassium, representing the main portion of that which is readily available to plants, makes up only a small part of the total potassium of soils. The great bulk is present in difficultly available forms, largely as a constituent of muscovite and feldspar; a small portion exists in nonexchangeable, but acid-soluble or fixed, forms and, as such, exhibits moderate availability to plants. Appreciable transformations of these less readily available forms to the exchangeable form occur in soils subjected to intensive cropping. A measure of the rate of these transformations is sometimes called "the potassium-supplying power of soils" and should be given consideration in formulating programs of potassium fertilization.

A large proportion of the cultivated soils of Wisconsin are cropped to grasses and legumes to supply forage for dairy cattle. Many of these soils have received little fertilizer other than manure, yet some have maintained good stands of high-quality hay for many years. With other soils, apparently of low potassium-supplying power, it has been increasingly necessary in recent years to make rather heavy applications of potash fertilizer in order to maintain high yield and quality. Accordingly, the relative capacity of six important soil types, including cropped and virgin samples, to supply crops with potassium from exchangeable and nonexchangeable forms was investigated, and the results are reported in this paper.

## LITERATURE REVIEW

Studies pertaining to the interrelationships between exchangeable and nonexchangeable forms of potassium and their relative availabilities to plants have been made by Fraps (10), Hoagland and Martin (11), Abel and Magistad (1), Bear, Prince, and Malcolm (5), Chandler, Peech, and Chang (7), and others. Most of these investigators found that, with cropping, soils release varying amounts of nonexchangeable potassium.

The exact nature of the mechanisms involved in the reciprocal transformations of exchangeable and nonexchangeable potassium is not known, although a number of explanations have been suggested for the phenomenon. DeTurk, Wood, and Bray (6, 8, 16) recognized four forms of potassium in soils, namely, water-soluble, exchangeable, fixed, and primary mineral. They believed that the first three forms tend to attain an equilibrium with one another so that when a soluble potassium salt is applied to the soil a shift occurs in the direction of the fixed forms, and when potassium is removed by cropping a shift occurs

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in the fixed forms to the water-soluble and exchangeable forms. They considered the fixed potassium to exist in two forms, one being dissolved by boiling for 10 minutes in  $N HNO_3$ , and the other being insoluble under this treatment. They found that the quantity of the soluble forms present was directly related to the potassium-supplying power of the soil. Their results suggested that potassium fixation is desirable, since fixed potassium is not subject to leaching and becomes available to crops on depletion of the more available forms.

Alternate freezing and thawing treatments were shown by Fine, Bailey, and Truog (9) to liberate as much as 150 pounds of potassium per acre from nonexchangeable forms in some soils. That alternate wetting and drying of potassium-fertilized soils caused fixation of potassium in nonexchangeable forms was demonstrated by N. J. Volk (15) in 1934, and later by G. W. Volk (14) and Truog and Jones (13).

In 1945, Martin, Overstreet, and Hoagland (12) working with California soils, found indications that a number of cations might be involved in the transformation of exchangeable potassium to nonexchangeable forms. They found increases in the amounts of exchangeable calcium, magnesium, and sodium present when potassium fixation occurred.

Attoe and Truog (2) in 1945 proposed that the potassium of soils be divided into three categories as regards availability to plants; namely, the readily available or water-soluble and exchangeable forms of potassium, the moderately available or fixed and biotite forms, and the difficultly available or feldspar and muscovite forms. The moderately available forms of potassium were those that were nonexchangeable but soluble when treated for 1 hour with 0.5  $N HCl$ .

Attoe (3) reported in 1946 that when six moist, unfertilized cropped soils were dried at room temperature, increases of 4 to 90 per cent in the contents of exchangeable potassium resulted. Conversely, he found fixation to occur when these soils were fertilized with potassium and stored in the moist condition for 2 months. Additional fixation occurred when these soils were dried. Addition of lime and potassium fertilizer to a Spencer soil with subsequent storage for 2 years in the moist condition resulted in the fixation of up to 32 per cent of the applied potassium, compared to a fixation of only 5 per cent in fertilized but unlimed soil similarly stored. Additional potassium was fixed in each case when the soils were dried.

#### MATERIALS AND METHODS

Six important Wisconsin soils, namely, Carrington silt loam, Miami silt loam, Spencer silt loam, and Plainfield sand from both virgin and cropped fields, and Antigo silt loam and Superior clay loam from cropped fields only were used. The pH, content of exchangeable potassium, and base-exchange capacity of each of these soils are given in table 1. For the pot tests, all soils except the Plainfield were diluted with an equal weight of quartz sand to shorten the time necessary to crop out the potassium. The soils were then placed in  $\frac{1}{2}$ -gallon pots, each treatment being represented by three replicates.

Suitable amounts of nutrients other than potassium were supplied to all pots from time to time during the 9-month cropping period. Four crops of oats were grown on all of the soils receiving the various treatments and were harvested at the dough stage. For comparison, Ladino clover was also grown on six of the soils, which were limed to pH 6.5 for both oats and clover. Six cuttings of Ladino clover were made at the early flowering stage. The harvested plant material was dried and weighed, and the content of potassium determined. The content of exchangeable potassium in the soils was determined before and after the cropping period. The amount of nonexchangeable potassium released and absorbed by the crops was assumed to be the difference between the decrease

in the exchangeable potassium content of the soil and the total amount of potassium removed by the crops. These data were converted to an acre plow layer of 2,000,000 pounds of the diluted soils as such, except as otherwise specified. Potassium was determined in all cases by means of the flame photometer (4).

#### UPTAKE OF POTASSIUM BY OATS AND CLOVER FROM CROPPED AND VIRGIN SOILS

Since the uptake of potassium by plants is not only a function of the supplying power of the soil but also a function of the feeding power of the plant itself, two different crop plants, namely, oats and Ladino clover, were grown. Although oats can make a normal growth in the presence of relatively high

TABLE 1  
*pH, content of exchangeable potassium, and base-exchange capacity of six soil types*

SOIL TYPE	CROPPED OR VIRGIN	pH OF SOIL	EXCHANGEABLE POTASSIUM	BASE-EXCHANGE CAPACITY
			<i>lb./A.</i>	<i>m.e./100 gm.</i>
Carrington silt loam	Cropped	5.70	138	17.0
	Virgin	5.73	245	19.9
Miami silt loam	Cropped	6.86	149	16.2
	Virgin	6.70	551	20.7
Spencer silt loam	Cropped	5.15	75	4.7
	Virgin	5.05	118	6.6
Plainfield sand	Cropped	6.38	121	3.5
	Virgin	5.85	86	2.6
Antigo silt loam	Cropped	5.00	91	11.1
Superior clay loam	Cropped	6.55	128	8.3

acidities, Ladino clover requires a soil reaction near neutral for optimum growth. For this reason, the soils used in this experiment were limed.

Of the soils listed in table 1, those having an original pH value below 6.0 were used in this phase of the investigation. These soils were limed to pH 6.5 by adding a mixture consisting of 4 parts of  $\text{CaCO}_3$  to 1 of  $\text{MgCO}_3$  by weight. The amounts needed by each soil were determined in a series of tests in which increasing amounts of  $\text{Ca}(\text{OH})_2$  in solution were added to samples of the soils; after 2 days, the pH values of the soils were determined and the amounts of lime needed were calculated accordingly.

Rather severe potassium-deficiency symptoms were noted on most of the Ladino clover plants of the first cutting grown on the Spencer and Antigo cropped soils. Similar deficiency symptoms were first observed on plants of the second cutting grown on the Plainfield and Spencer virgin soils, on plants of the fourth cutting grown on the Carrington cropped soil, and on plants of the sixth cutting grown on the Carrington virgin soil. These deficiency symptoms became more

pronounced as the cropping period progressed. Chemical analyses of the crops indicated that Ladino clover exhibits rather severe potassium-deficiency symptoms when its potassium content, expressed on the dry tissue basis, becomes less than 0.5 per cent. Chandler, Peech, and Chang (7) reported the first appearance of these potassium-deficiency symptoms on Ladino clover leaves when the potassium content of the oven-dry tissue fell below 0.8 per cent.

The potassium content of both oats and Ladino clover grown on each of the soils decreased with cropping. This decrease for the crops grown on the virgin

TABLE 2

*Exchangeable and nonexchangeable potassium removed by four crops of oats and six cuttings of Ladino clover from soils limed to pH 6.5 during a cropping period of 9 months*

SOIL TYPE*	CROPPED OR VIRGIN	CROP GROWN	POTASSIUM REMOVED BY CROPS†		RATIO OF UPTAKE OF NONEXCHANGEABLE POTASSIUM CLOVER/OATS
			Exchangeable plus nonexchangeable	Non-exchangeable	
			lb./A.	lb./A.	
Carrington silt loam	Cropped	Oats	98	68	1.31
		Clover	119	89	
	Virgin	Oats	142	63	1.70
		Clover	201	107	
Spencer silt loam	Cropped	Oats	54	47	1.00
		Clover	59	47	
	Virgin	Oats	70	36	1.19
		Clover	79	43	
Plainfield sand	Virgin	Oats	88	22	1.27
		Clover	92	28	
Antigo silt loam	Cropped	Oats	57	43	0.79
		Clover	59	34	

\* All soils except Plainfield sand were diluted 1:1 by weight with white quartz sand, and results are given on diluted basis.

† Average of three replicates.

Carrington soil ranged from 1.53 per cent in the first crop of oats to 0.46 per cent in the fourth crop, and from 0.86 per cent in the first cutting of Ladino clover to 0.50 per cent in the sixth cutting. Similar results were obtained for the other soils. The much larger percentage of potassium contained in the first crop of oats compared to that in the first cutting of Ladino clover is apparently due to the larger yield of clover (8,350 pounds per acre) compared to that of oats (3,300 pounds per acre).

The amounts of total and nonexchangeable potassium removed from the soils during the 9-month period by the oats and the Ladino clover are given in table 2. Rather large amounts of nonexchangeable potassium were removed by both oats and clover from the Carrington soils. For example, 107 pounds



per acre were removed by clover from the Carrington virgin soil even after dilution with equal parts of sand. Less than half this amount was removed from the Spencer cropped, Spencer virgin, and Antigo cropped soils, all similarly diluted with sand. Even though the Plainfield virgin soil was undiluted, it supplied only 22 and 28 pounds per acre of nonexchangeable potassium to oats and clover, respectively.

In the Carrington virgin soil, Ladino clover removed 1.7 times as much potassium from nonexchangeable forms as did oats. These removals were also larger for clover than for oats grown on the Carrington cropped, the Plainfield virgin, and the Spencer virgin soils. Equal quantities of nonexchangeable potassium were removed by oats and clover from the Spencer cropped soil, whereas from the Antigo cropped soil more nonexchangeable potassium was removed by oats than by clover. These results indicate that Ladino clover is superior to oats in removing nonexchangeable potassium from soils containing relatively large amounts of exchangeable potassium and has a relatively poor feeding power at low levels of exchangeable potassium. This is further evidenced by the larger decreases in uptake by successive crops of clover than of oats. Thus, the potassium removed per acre by clover grown on the Carrington virgin soil ranged from 72 pounds in the first cutting to 13 pounds in the sixth cutting, compared to a decrease for oats grown on this soil from 51 pounds for the first crop to 27 pounds for the fourth crop, the length of cropping period being the same as for clover. The lower efficiency of clover as compared to oats in feeding on potassium at low levels of exchangeable potassium was evidenced by the smaller growth, thinning stands, and lower potassium content of the former crop.

#### INFLUENCE OF LIMING ACID SOILS ON UPTAKE OF POTASSIUM BY OATS

As has been mentioned, the acid soils used in the previous experiment were limed to pH 6.5 for that experiment. To investigate the influence of liming acid soils on the uptake of potassium by crops, oats were also grown at the same time on these soils without lime in a series of cultures otherwise exactly parallel to the limed series. The results of both the unlimed and the limed series are given in table 3.

In every case, the uptake of nonexchangeable potassium by oats was somewhat greater from the unlimed soils, the increase being due to slightly higher yields (average of 8 per cent higher) and a somewhat higher potassium content of the crops grown on the unlimed soils. These results indicate that the capacity of soils to supply nonexchangeable potassium for absorption by plants is repressed by the addition of lime. This effect, however, is often beneficial because it retards or prevents a luxury consumption of potassium by plants where the exchangeable potassium is in excess of plant needs. It is interesting to note the relative magnitudes of this repression between the respective cropped and virgin soils. In the three virgin soils, the amounts of nonexchangeable potassium released from the unlimed soils were 1.39 to 1.56 times those from the respective limed soils; whereas in the three cropped soils, the amounts released from the

unlimed soils were only 1.06 to 1.12 times those from the corresponding limed soils.

The low release ratios of the cropped soils indicate not that lime had little effect on release, but rather that the supplies of nonexchangeable potassium were probably low, and therefore the repression effect of lime had little chance to exert itself. It appears then that in the virgin soils, relatively large quantities of nonexchangeable potassium were released to the plants where no lime was used, but were conserved for future crops when lime was added.

TABLE 3  
*Influence of liming acid soils upon exchangeable and nonexchangeable potassium removed by four crops of oats*

SOIL TYPE*	CROPPED OR VIRGIN	UNLIMED OR LIMED	pH BEFORE AND AFTER CROPPING	POTASSIUM REMOVED BY FOUR CROPS†		RATIO OF RELEASE OF NONEXCHANGEABLE POTASSIUM, UNLIMED/LIMED
				Exchangeable plus nonexchangeable	Non-exchangeable	
				lb./A.	lb./A.	
Carrington silt loam	Cropped	Unlimed	5.7-5.0	104	73	1.07
		Limed	6.5-5.9	98	68	
	Virgin	Unlimed	5.7-5.0	162	86	1.39
		Limed	6.5-6.2	142	62	
Spencer silt loam	Cropped	Unlimed	5.2-4.6	61	50	1.06
		Limed	6.5-5.6	54	47	
	Virgin	Unlimed	5.1-4.2	92	56	1.56
		Limed	6.5-5.4	70	36	
Plainfield sand	Virgin	Unlimed	5.9-4.6	95	32	1.46
		Limed	6.5-5.6	88	22	
Antigo silt loam	Cropped	Unlimed	5.0-4.4	67	48	1.12
		Limed	6.5-5.5	57	43	

\* All soils except Plainfield sand were diluted 1:1 by weight with white quartz sand.

† Average of three replicates.

#### INFLUENCE OF REMOVAL OF EXCHANGEABLE POTASSIUM ON CAPACITY OF SOILS TO SUPPLY OATS WITH NONEXCHANGEABLE POTASSIUM

Soils that contain large amounts of exchangeable potassium ordinarily require long periods of cropping before a knowledge of their capacity to supply nonexchangeable potassium for plant absorption can be determined. To accelerate a test of this supplying power by several soils, some of their exchangeable potassium was removed prior to cropping by leaching with a  $\text{CaCl}_2\text{-MgCl}_2$  solution.

All of the soils listed in table 1 were included in this experiment. Four-gallon glazed earthen pots provided with drainage outlets were used as leaching vessels. A 3-inch layer of gravel covered with cheesecloth was placed in the bottom of each pot, and over this, 7 kgm. of the sand-soil mixture to be leached. The



soils were leached intermittently with 1-liter portions of a solution 0.4 *N* with respect to  $\text{CaCl}_2$  and 0.1 *N* with respect to  $\text{MgCl}_2$ . Fifty liters were added to each pot, after which the excess of salts was removed by washing with distilled water until the leachate was virtually free of chlorides. The surfaces of the soils were kept moist at all times while the leachate was allowed to drip from the vessels at a rate of approximately two drops per second.

After the leaching treatment, the soils were removed from the pots and allowed to dry to field capacity. Each soil was then sieved, a sample taken for analysis,

TABLE 4

*Influence of removal of part of the exchangeable potassium of soils by leaching with a  $\text{CaCl}_2$ - $\text{MgCl}_2$  solution on their capacity to supply nonexchangeable potassium to four crops of oats*

SOIL TYPE*	CROPPED OR VIRGIN	EXCHANGEABLE POTASSIUM		NONEXCHANGEABLE POTASSIUM REMOVED BY FOUR CROPS†	
		In unleached soils	In soils leached with $\text{CaCl}_2$ - $\text{MgCl}_2$ solution	From soils not previously leached	From soils previously leached with $\text{CaCl}_2$ - $\text{MgCl}_2$ solution
		lb./A.	lb./A.	lb./A.	lb./A.
Carrington silt loam	Cropped	69	54	73	77
	Virgin	123	61	86	98
Miami silt loam	Cropped	75	56	107	130
	Virgin	276	75	48	150
Spencer silt loam	Cropped	38	36	50	58
	Virgin	59	32	56	56
Plainfield sand	Cropped	121	40	36	59
	Virgin	86	31	32	42
Antigo silt loam	Cropped	46	35	48	57
Superior clay loam	Cropped	64	45	71	72

\* All soils except Plainfield sand diluted 1:1 by weight with white quartz sand.

† Average of three replicates.

potted, and cropped to four plantings of oats. For comparison, the unleached soils were similarly cropped during the same period.

The amounts of nonexchangeable potassium absorbed by the four crops of oats are given in table 4, which includes some of the data reported in table 3. Except for the Spencer soil, the amount of nonexchangeable potassium absorbed by the crops from each of the leached soils is larger than that absorbed from the corresponding unleached soils, the amounts ranging up to three times as much, in the Miami virgin soil. The reason for this difference appears to lie in the effect of the leaching treatment on the reduction of the content of exchangeable potassium from 276 to 75 pounds per acre (table 4) and its subsequent effect on

increasing the rate of transformation of potassium from the nonexchangeable to the exchangeable form.

It appears, therefore, that in determinations of the capacities of soils to supply crops with nonexchangeable potassium, the contents of exchangeable potassium should be similar in all of the soils at the beginning of the cropping period. This condition can be attained by leaching the soils with a suitable salt solution, as already described, or by cropping the soils to remove excessive amounts of exchangeable potassium before the test crop is grown. The former method saves time.

#### POTASSIUM-FIXING POWER OF SOILS

The investigations that follow were made to determine the relative capacity of the soils used in the previous experiments to fix added soluble potassium in nonexchangeable form. That drying after such addition causes fixation and, furthermore, affords a rapid method of attaining equilibrium between the added, exchangeable, and nonexchangeable forms of soil potassium was demonstrated by Attoe (3) and others. Accordingly, to portions of each of the soils, a solution of KCl was added at the rate of 900 pounds of potassium per acre. The soils were then dried at 80°C. for 14 days. Determinations of exchangeable potassium were made before the addition and after the drying treatment.

The amount and the percentage of applied potassium fixed by drying are given in table 5. Fixation of applied potassium ranged from 12 per cent in the virgin Plainfield to 59 per cent in the virgin Miami soil. Although the rate of fixation is not strictly correlated with any single soil characteristic, there appears to be a definite relation between it and the pH and/or base-exchange capacity. In every case, the soils which fixed relatively large amounts of potassium were characterized by relatively high pH values and/or relatively high base exchange capacities. It is of special interest to note that the virgin Miami soil which has the highest fixing capacity of the soils tested, also has the highest potassium-supplying power (table 4).

#### RECOVERY OF ARTIFICIALLY FIXED POTASSIUM BY OATS

Experiments based on the principle of varying fertility levels have been started on certain soils in Wisconsin. To attain some of these desired levels, it was necessary to make an initial application of potassium equal to as much as 1,300 pounds of 50 per cent muriate per acre. Undoubtedly, part of this potassium has become fixed in nonexchangeable form. The question arises as to the availability of this fixed form to subsequent crops. Accordingly, an experiment was set up to determine the rate of recovery of artificially fixed potassium by oats.

Seven kilograms of each soil was treated with a solution of KCl at the rate of 900 pounds of potassium per acre. The soils were then dried at 80°C. for 14 days. After this fixation treatment, the soils, with the exception of Plainfield sand, were diluted 1:1 with quartz sand. They were then leached with a  $\text{CaCl}_2$ - $\text{MgCl}_2$  solution in accordance with the method previously described. This

treatment reduced the content of exchangeable potassium to amounts similar to those given in table 4 for the unfertilized leached soils, and therefore reduced the amount of potassium that needed to be removed by cropping. Also, following this treatment, suitable amounts of nitrogen, phosphorus, and minor elements were applied to the soils, which were then planted to four successive crops of oats.

The potassium removed by the crops was obtained from three sources: exchangeable, as evidenced by the decrease during cropping; artificially fixed; and naturally occurring fixed forms of soil potassium. The total nonexchangeable

TABLE 5

*Capacity of soils\* to fix potassium added as KCl, in nonexchangeable form when dried at 80° for 14 days*

SOIL TYPE	CROPPED OR VIRGIN	POTASSIUM AFTER ADDITION OF 900 POUNDS			PERCENTAGES OF APPLIED POTASSIUM FIXED
		Exchangeable + water-soluble		Fixed upon drying	
		Before drying	After drying		
		lb./A.	lb./A.	lb./A.	
Carrington silt loam	Cropped	1038	593	445	49
	Virgin	1145	699	446	49
Miami silt loam	Cropped	1049	652	397	44
	Virgin	1451	920	531	59
Spencer silt loam	Cropped	975	612	363	40
	Virgin	1018	763	255	28
Plainfield sand	Cropped	1021	881	140	16
	Virgin	986	875	111	12
Antigo silt loam	Cropped	991	707	284	32
Superior clay loam	Cropped	1028	522	506	56

\* See table 1 for pH and base-exchange capacity.

or fixed potassium released to the crops was determined by subtracting the decrease in exchangeable with cropping from the total potassium uptake. Then the difference between the amounts of nonexchangeable potassium released from these soils and those soils not subjected to the fixation treatment but similarly leached with a  $\text{CaCl}_2\text{-MgCl}_2$  solution (see table 4) gave the amount of artificially fixed potassium removed by the oats.

In most cases, each successive crop contained a smaller percentage of potassium than the previous crop, with the most abrupt drop occurring between the first and second crops. For example, the potassium content of the crops grown on the Miami cropped soil ranged from 2.66 per cent for the first crop to 0.69 per cent for the fourth crop. Similar decreases were obtained for the other soils.

The percentages of artificially fixed potassium removed by the four crops of oats from all the soils are given in table 6. Of the artificially fixed potassium 24 to 47 per cent was recovered in the 9-month cropping period. On Superior clay loam, a rather low percentage of recovery was obtained. This can be attributed to the restricted growth due to the poor physical condition of the soil. A relatively high recovery occurred on the Plainfield virgin soil. As previously shown, this soil contained very low amounts of naturally fixed potassium. Under such conditions, the artificially fixed forms would be the chief source of

TABLE 6  
*Recovery of artificially fixed\* potassium by four crops of oats from soils*

SOIL TYPE	CROPPED OR VIRGIN	ARTIFICIALLY FIXED POTASSIUM		PERCENTAGES OF ARTIFICIALLY FIXED POTASSIUM RECOVERED IN OATS
		Contained in the soils	Removed by oats	
		<i>lb./A.</i>	<i>lb./A.</i>	
Carrington silt loam	Cropped	223	101	45
	Virgin	224	93	42
Miami silt loam	Cropped	199	79	40
	Virgin	266	86	32
Spencer silt loam	Cropped	183	54	30
	Virgin	123	39	32
Plainfield sand	Cropped	140	33	24
	Virgin	111	52	47
Antigo silt loam	Cropped	143	55	38
Superior clay loam	Cropped	253	62	25

\* "Artificially fixed" refers to potassium made nonexchangeable by drying at 80°C. after fertilization with KCl at the rate of 900 pounds of potassium per acre.

potassium for the plants, and hence a high percentage of recovery would be expected.

The lower percentage of recovery from the Miami virgin than from the cropped soil is probably due to the larger amount of potassium fixed by the virgin sample.

It is important to note that the percentage recoveries from the Antigo cropped, Spencer cropped, and Spencer virgin soils were almost as high as those from the Miami and Carrington soils, even though the actual amounts fixed and recovered were less. This would tend to indicate that even though different soils are capable of fixing varying amounts of added potassium, the release to plants is somewhat proportional to the amounts fixed. Accordingly, a large portion of the potassium that is fixed in nonexchangeable form when added as fertilizer is readily recoverable by plants in relatively short cropping periods. Because of this, the power of soils to fix potassium when present in excess and to release



it as needed may be thought of as an extremely beneficial property, without which much of the potassium added as fertilizer might well be lost by leaching.

#### SUMMARY

A study was made of the rate of change of potassium from nonexchangeable or fixed forms to the exchangeable form in cropped and virgin soils as measured by the amounts of potassium removed by four crops of oats and six cuttings of Ladino clover grown on these soils in pot cultures. The effects of liming to pH 6.5, removal of exchangeable potassium by leaching with a  $\text{CaCl}_2\text{-MgCl}_2$  solution, and fixation due to drying on this removal by oats from different soils were also investigated. The results of these studies are summarized as follows:

1. Ladino clover removed 1.2 to 1.7 times as much nonexchangeable potassium as did oats from four of the soils in which the original levels of exchangeable potassium were relatively high, whereas oats, because of their capacity to grow well at rather low levels of available potassium, were either equal to or superior to the clover in this respect in the other two soils in which the contents of exchangeable potassium were relatively low.

2. In every case, liming of acid soils repressed the amounts of total and nonexchangeable potassium removed by oats. This effect, however, is often beneficial because it conserves the exchangeable and fixed forms of potassium, where they are present in relatively large amounts, by retarding or preventing a luxury consumption of this element by plants.

3. When the soils were leached with a  $\text{CaCl}_2\text{-MgCl}_2$  solution to reduce the content of exchangeable potassium prior to cropping, increases up to three times as much nonexchangeable potassium were absorbed from them by four crops of oats as from the unleached soils.

4. When the soils were fertilized with KCl at the rate of 900 pounds of potassium per acre and dried at  $80^\circ\text{C}$ . for 14 days, potassium became fixed in amounts ranging from 12.0 to 59.0 per cent of that applied. In every case, high fixing power for potassium was closely associated with high supplying power of nonexchangeable potassium to crops and high pH and/or high base-exchange capacity.

5. That this fixed potassium becomes available to a considerable degree for crop use under suitable conditions is indicated in the recovery, by four crops of oats in pot cultures, of 24 to 47 per cent of the amounts fixed.

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# BORON CONTENT AND REQUIREMENTS OF WEST VIRGINIA SOILS<sup>1</sup>

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The study reported in this paper was initiated in 1946 to determine the available-boron content of West Virginia soils, to determine the effect of boron applications on the growth of alfalfa, and to study the interaction effects of calcium and potassium on the boron requirements of alfalfa.<sup>3</sup>

## AVAILABLE BORON IN WEST VIRGINIA SOILS

### *Methods*

Soil samples were collected from 13 counties in West Virginia representing 23 soil types important to agriculture in the state. Most of the samples were collected from alfalfa fields containing stands of varying ages and quality. The samples in most cases were taken at two depths: the first, representing the plow layer, approximately 0 to 8 inches; and the second, from the subsoil, approximately 10 to 20 inches. These soils were analyzed for available boron by the method of Berger and Truog (1). Determinations of soil pH were also made.

In an attempt to obtain a more complete knowledge of the boron content and supplying power of these soils than is possible with chemical analysis alone, the soils were also tested by the biological method of Colwell (4).

### *Results and discussion*

*Chemically available boron.* The results of the analysis for available boron in the soils are presented in table 1. The data indicate that none of the soils analyzed were extremely low in available boron. The available boron content of the plow layer was below 0.30 p.p.m. in only two samples. Many of the soils, however, contained in the plow layer a supply of available boron which ranged from 0.30 to 0.35 p.p.m. Work in the northeastern part of the United States (4, 5, 12) has indicated that a boron content approaching 0.35 p.p.m. available boron is the lower limit at which maximum alfalfa yields are obtained. Thus it appears that, at present, most West Virginia soils contain sufficient available boron to prevent serious boron deficiency in alfalfa. Many of the soils, however, are near or are approaching the lowest limit for maximum alfalfa growth.

<sup>1</sup> Part of a thesis presented to the Graduate School at West Virginia University in partial fulfillment of the requirements for the degree of doctor of philosophy. Published with the approval of the director of West Virginia Agricultural Experiment Station as Science Paper No. 393.

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<sup>3</sup> In view of the availability of such extensive literature reviews as "Boron as a Plant Nutrient," including supplements published at intervals by the American Potash Institute, Inc., only work pertinent to this report is cited herein.

TABLE 1

*Available boron in a number of West Virginia soils*

SAMPLE NO.	COUNTY	SOIL TYPE	DEGREE* OF SOIL LEACHING	pH		AVAILABLE B	
				Flow Layer	Sub-Soil	Flow Layer	Sub-soil
						p.p.m.	p.p.m.
<i>Soils from acid shale and sandstone</i>							
4	Nicholas	Gilpin silt loam	M	5.85	5.52	0.35	0.23
6	Nicholas	Cookport silt loam	VS	7.39	5.20	0.35	0.28
24	Monongalia	Cookport silt loam	VS	6.66	6.13	0.38	0.30
8	Greenbrier	Cookport fine sandy loam	VS	5.73	4.60	0.28	0.25
9	Greenbrier	Cookport fine sandy loam†	VS	6.87	5.02	0.30	0.28
1	Wetzel	Meigs silt loam	M	6.30	4.70	0.48	0.26
5	Nicholas	Clymer silt loam	M	5.11	4.67	0.33	0.25
7	Greenbrier	Calvin silty clay loam	M	5.65	4.74	0.34	0.30
35	Monongalia	Rayne silt loam	S	5.10	....	0.33	....
36	Monongalia	Rayne silt loam	S	4.40	....	0.35	....
38	Summers	Rardon silt loam†	M	6.30	....	1.75	....
39	Summers	Rardon silt loam†	M	6.70	....	2.00	....
<i>Soils from calcareous shales</i>							
27	Hardy	Litz shaley silt loam	SI	6.31	4.75	0.50	0.38
21	Wetzel	Upshur silty clay	SI	6.66	5.91	0.40	0.23
23	Wetzel	Upshur silty clay	SI	6.32	4.65	0.32	0.23
40	Grant	Upshur silty clay	SI	5.44	....	0.33	....
<i>Soils from limestone</i>							
28	Jefferson	Hagerstown silt loam	SI	6.71	5.90	0.35	0.23
29	Jefferson	Hagerstown silt loam	SI	6.63	5.97	0.35	0.28
29A	Jefferson	Hagerstown silt loam	SI	6.57	....	0.34	....
30	Jefferson	Hagerstown silt loam	SI	7.15	6.45	0.40	0.25
15	Greenbrier	Pickaway cherty silt loam†	VS	6.57	4.66	0.85	0.50
16	Greenbrier	Pickaway cherty silt loam	VS	7.07	....	0.38	....
12	Greenbrier	Frankstown silt loam†	S	6.60	5.80	0.88	0.28
12A	Greenbrier	Frankstown silt loam	S	6.77	....	0.33	....
13	Greenbrier	Frankstown silt loam†	S	6.74	5.52	0.88	0.40
14	Greenbrier	Frankstown silt loam†	S	7.08	5.26	0.32	0.23
32	Berkeley	Frankstown silt loam†	S	7.40	6.45	0.53	0.25
34	Berkeley	Frankstown silt loam	S	6.20	....	0.40	....
31	Berkeley	Frederick cherty silt loam	S	6.47	4.81	0.35	0.23
33	Berkeley	Berkeley silty clay loam	None	6.89	6.55	0.38	0.28
10	Monroe	Tumbez silty clay	None	7.12	....	0.63	....
11	Monroe	Chilhowie silty clay	None	7.34	7.19	0.55	....
<i>Terrace soils from acid shales and sandstone</i>							
18	Putnam	Monongahela fine sandy loam†	VS	7.00	6.02	0.29	0.25
25	Hardy	Monongahela fine sandy loam	VS	5.90	4.92	0.32	0.20
37	Monongalia	Monongahela fine sandy loam	VS	4.60	....	0.35	....
17	Putnam	Zoar silty clay loam	S	6.81	4.93	0.35	0.30
3	Nicholas	Blago silt loam	SI	4.35	4.52	0.32	0.28

TABLE 1.—*Continued*

SAMPLE NO.	COUNTY	SOIL TYPE	DEGREE* OF SOIL LEACHING	pH		AVAILABLE B	
				Plow Layer	Sub-Soil	Plow Layer	Sub-soil
						p.p.m.	p.p.m.
		<i>Flood plain soils</i>					
2	Braxton	Moshannon silt loam	Sl	6.10	5.32	0.35	0.35
26	Hardy	Sequatchie silt loam	Sl	6.30	5.65	0.49	0.55
		<i>Ohio River terrace</i>					
20	Wetzel	Wyatt silty clay loam	M	6.87	4.57	0.34	0.23
19	Mason	Wheeling fine sandy loam†	S	7.31	6.85	0.75	0.25
22	Wetzel	Wheeling fine sandy loam	S	5.12	5.02	0.32	0.23

\* VS = very strong; S = strong; M = moderate; Sl = slight.

† Boron-deficiency symptoms observed in the field.

‡ Field treated with 20 pounds borax per acre.

The data show that the available boron contents of the subsoils are somewhat lower than those of the plow layer. This would indicate that the surface layer is the more important source of boron and that a shortage may be more likely to occur on badly eroded soils.

It is evident from the data in table 1 that the soils lowest in available boron and most likely to benefit from boron fertilization are those which have been subject to strong or very strong leaching. The largest group in this category are residual soils derived from acid gray shale and sandstone, and terrace soils which originated on alluvium from these materials. The Cookport and Monongahela soils are representative of these groups. Frankstown, a strongly leached soil developed on limestone, is also low in available boron and should be included with the soils most likely to benefit from boron fertilization.

Alfalfa plants in the field on these highly leached soils have, in the observations made, frequently shown boron-deficiency symptoms, and those plants which have been chemically analyzed were found to be low in total boron.

*Biologically available boron.* The calibration age values obtained in the sand cultures at each boron level agreed very closely with those obtained by Colwell (4). The average age values of the 0.30 p.p.m. and the 0.50 p.p.m. boron-quartz-sand cultures were found to be 37 and 41 days respectively.

The age values obtained for all the soils tested by this method were found to be greater than 40 days. This would indicate that these soils contained a supply of available boron sufficiently high for growing alfalfa. The available boron contents of the soils obtained by the biological method were higher, however, than those obtained by chemical analysis. This appears to be the result of various soil factors, such as acidity, lack of fertility, and poor physical properties, which caused a much slower rate of growth in the soil cultures than occurred in the quartz sand cultures. The slower growth would remove less boron than where growth was rapid, the appearance of deficiency symptoms would be delayed, and the boron content thus indicated for the soils would be relatively high.

It appears, therefore, that the biological method, as outlined by Colwell (4),



is limited in its application for determining available boron in many West Virginia soils. For satisfactory results, the soils must be well limed, fertile, and possess good physical properties. As to the soils tested in this study, the only conclusion that can be made on the basis of the biological method is that none appeared to be severely deficient in boron.

#### EFFECT OF BORON ON GROWTH OF ALFALFA IN GREENHOUSE

This part of the investigation deals primarily with a quantitative study of the yield response and chemical composition of alfalfa grown in pot cultures, as affected by boron treatments, at varying known levels of calcium and potassium.

#### *Soils used and cultural and chemical methods employed*

Two important West Virginia soil types were used in this investigation; namely, Rayne silt loam and Monongahela silt loam. The analyses of these soils are given in table 2.

TABLE 2

*Chemical analysis of the Rayne and Monongahela soils used in greenhouse experiments*

	RAYNE SILT LOAM (NO. 1)	RAYNE SILT LOAM (NO. 2)	MONONGAHELA SILT LOAM
pH.....	5.10	4.30	4.60
Available P..... <i>lb./A.</i>	32.0	24.0	14.0
Available boron..... <i>p.p.m.</i>	0.33	0.35	0.35
Exchange capacity..... <i>m.e./100 gm. soil</i>	7.08	6.00	6.69
Total exchangeable bases..... <i>m.e./100 gm. soil</i>	3.30	0.45	1.00
Exchange calcium..... <i>m.e./100 gm. soil</i>	3.17	0.40	0.90
Organic matter..... <i>per cent</i>	2.60	2.49	2.11

Rayne silt loam is a strongly leached upland soil derived from acid gray shale and sandstone. Monongahela silt loam is a strongly leached terrace soil developed on alluvium derived from acid gray shale and sandstone. Both soils were thought to be low in boron. The Rayne soil, from an earlier study (10), was known to be particularly susceptible to injury from overliming.

Two different samples of Rayne silt loam were used: sample No. 1 was taken from a cultivated field; and sample No. 2, from a nearby untreated permanent pasture.

The soils were collected from the surface 6 inches, screened through a  $\frac{1}{4}$ -inch mesh screen, and thoroughly mixed. Chemically pure calcium carbonate was then applied to quantities of soil to bring the pH to approximately 6.5, 7.0, and 7.5. The soils were remixed, moistened, and let stand for 1 month to allow the lime and soil to reach equilibrium.

Samples were then taken for pH determinations, and chemically pure mono-calcium phosphate, potassium chloride, and commercial borax were applied to



each set of replicates according to the desired treatment. After thorough mixing, 7,000-gm. quantities of air-dry soil were weighed into 2-gallon glazed earthenware pots.

Inoculated Grimm alfalfa was planted in each pot, and by the end of 6 weeks all were thinned to 12 plants per pot. A uniform moisture content was maintained throughout the experiment by periodic weighings.

This experiment was started in the greenhouse on December 20. The first cutting was made on April 3, and the remaining cuttings were made when the alfalfa was in bloom, at approximately 5-week intervals. Some artificial light was supplied from January 15 to March 15. The pots at all times were arranged on the greenhouse bench in a randomized block design.

All alfalfa plant samples were oven-dried, weighed, and ground in a micromill for chemical analysis. The alfalfa obtained from each pot in the first three cuttings was analyzed for calcium and potassium, and all five cuttings were analyzed for boron. Boron determinations were made according to the method of Berger and Truog (1). Calcium was determined colorimetrically by the chlor-anilic acid method of Tyner (15). Potassium analyses were made by the method of Brown, Robinson, and Browning (3).

#### *Results and discussion*

*Potassium-boron series.* In this series a marked increase in yield resulted from the potash applications. The average increase for all K and 2K treatments was 39 and 59 per cent respectively. Borax, on the other hand, had no effect on yield. At no time during the growing of five crops was there any evidence of boron deficiency or toxicity. Potash-deficiency symptoms, however, did appear in the latter cuttings on the no-potash treatments.

The treatments used and the mean boron content of the alfalfa obtained in five cuttings are presented in table 3. This table shows that the addition of 20 pounds borax per acre approximately trebled the boron content of the plant tissue. The 2K treatment significantly decreased the boron content of the alfalfa tissue grown without borax. This may be a "dilution effect" caused by the increased yield produced by the potash. There was a small but not significant decrease on the borated pots.

It was of interest to note from the individual analysis of each cutting, that within each treatment the concentration of boron in the alfalfa tissue remained nearly constant throughout five cuttings. This, together with the fact that the crop removal was heavy, indicates that even though the available boron content without borax treatment was not high, the soil was able to supply considerable boron for a sustained period.

Table 4 gives the average boron, calcium, and potassium contents of the alfalfa obtained in the first three cuttings on this series. It is noted here that the potassium content of the alfalfa tissue was increased by both applications of potash. Calcium, which was held at a uniform level in the soil for all treatments, decreased in the plant tissue with each added increment of potash. These interaction

effects of calcium and potassium are normally expected and have been amply demonstrated by other workers (11, 13). The amounts of calcium and potassium found in the alfalfa tissue appeared to be unaffected by applications of boron.

*Lime-fertilizer series.* In this phase of the study alfalfa was grown on two soil types, Rayne silt loam (No. 2) and Monongahela silt loam.

On Rayne silt loam (No. 2) the use of phosphate and potash gave a very

TABLE 3

*Mean boron content of alfalfa, in p.p.m. dry matter, grown in pots on Rayne silt loam (No. 1) with potash and boron as variables\**

BORAX TREATMENT	POTASH TREATMENTS†			BORON MEAN
	None	K	2K	
	<i>p.p.m.B</i>	<i>p.p.m.B</i>	<i>p.p.m.B</i>	<i>p.p.m.B</i>
None	30.2	27.2	25.7	27.7 ± .577
20 lb. per A.	84.5	81.7 (S. E. = ±1.00)	81.2	83.5 ± .577
Potash mean	57.3	54.4 (S. E. = ±.707)	53.4	

\* Each value represents the mean of five cuttings and four replicates. All pots limed to pH 7.0 and treated with 200 pounds  $P_2O_5$  per acre.

† K = 125 pounds  $K_2O$  per acre.

2K = 250 pounds  $K_2O$  per acre.

TABLE 4

*Boron, calcium, and potassium content of alfalfa grown on Rayne silt loam (No. 1) with potassium and boron as variables*

TREATMENT*	PLANT ANALYSIS†		
	B	Ca	K
	<i>p.p.m.</i>	<i>per cent</i>	<i>per cent</i>
P	29	2.96	0.80
P-K	25	2.31	1.43
P-2K	22	2.06	1.78
P-B	83	2.74	0.82
P-K-B	78	2.30	1.27
P-2K-B	81	2.00	1.77

\* P = 200 pounds  $P_2O_5$  per acre; K = 125 pounds  $K_2O$  per acre; B = 20 pounds borax per acre.

† Each value represents the average of three cuttings and four replications.

marked increase in yield at all three lime levels. Twenty pounds of borax per acre in addition to these two fertilizers had no significant effect on the yield. This was true despite the fact that on the alfalfa which received phosphate and potash at the two heaviest lime levels, boron-deficiency symptoms were evident on the third crop and were also observed on some of the replications from all succeeding crops. These symptoms were mild and always occurred as the plants

were nearing maturity. This probably accounts for the fact that yields were not affected. The work of Brown, Munsell, and King (2) and of Dawson and Gustafson (5) indicates that deficiency symptoms in alfalfa caused by borderline soil deficiency may be corrected without significant effect on the yield.

When the Rayne soil was limed to pH 7.1 and higher, a marked reduction in yield occurred, indicating serious injury due to overliming. None of the treatments employed alleviated this injury to a significant degree. The injury decreased in the latter harvests but never completely disappeared even after five cuttings.

The treatments used and the mean boron contents of the alfalfa obtained in five cuttings on Rayne silt loam (No. 2) are summarized in table 5. This table shows that the application of 20 pounds of borax per acre increased the boron content

TABLE 5

*Mean boron content of alfalfa, in p.p.m. of dry matter, grown in pots of Rayne silt loam (No. 2) with lime and fertilizer as variables\**

FERTILIZER TREATMENT†	LIME TREATMENT			FERTILIZER MEAN
	L (pH6.7)	2L (pH7.1)	3L (pH7.4)	
	p.p.m.B	p.p.m.B	p.p.m.B	
None	33.6	30.0	32.0	31.9 ± .745
P-2K	26.6	19.0	18.6	21.4 ± .745
P-2K-B	86.6	74.3	74.3	78.4 ± .745
Lime Mean	49.0	41.1	41.7	
		(S. E. = ±1.29)		
		(S. E. = ±.705)		

\* Each value represents the mean of five cuttings and three replicates

† P = 200 pounds  $P_2O_5$  per acre; 2K = 250 pounds  $K_2O$  per acre; B = 20 pounds borax per acre.

of the alfalfa on the fertilized pots more than threefold. The use of phosphate and potash decreased the boron content as compared to the pots not fertilized. This would indicate that the boron content of the soil was too low to supply the additional boron needed for increased yield which resulted from the fertilizer. Furthermore, it was noted that this soil was able to maintain a more nearly constant boron concentration in the plant tissue throughout the five cuttings when boron was applied. This was especially noticeable in the third cutting, when the highest yield was obtained. On the L-P-2K treatment the boron content averaged 34, 28, 18, 29, and 25 p.p.m. respectively for the five cuttings. When boron was applied to this treatment the corresponding values were 89, 83, 85, and 91 p.p.m. boron.

As indicated previously under discussion of yields, the alfalfa which received phosphorus and potash but no boron showed mild boron-deficiency symptoms at the 2L and 3L lime levels. Table 5 shows that the boron content of this alfalfa averaged 19.0 and 18.6 p.p.m. respectively for the two lime levels. Since no

yield increase resulted when boron was added to this treatment, it appears that this may be a critical boron level.

Some critical values for the boron content of alfalfa plants have been established by recent investigations. Dawson and Gustafson (5) found 20 p.p.m. boron to be a critical level. Brown, Munsell, and King (2) obtained response in some cases and no response in others at 17 p.p.m. Dunklee and Midgley (7) indicated a need for boron at 15 p.p.m. Jordan and Powers (8) reported that 12 p.p.m. boron indicated deficient plants. Dregne and Powers (6) found deficient plants to contain 7.0 to 11.5 p.p.m. boron, whereas normal plants contained 12 to 22.5 p.p.m. boron. Rogers (14) reported 10 p.p.m. boron as a critical value on red and yellow podzolic soils of Alabama. Some of the variations between these values may be due to differences in soil type and climatic conditions.

Table 5 shows that as the calcium content of the soil was increased by additions of calcium carbonate to pH 7.1 the boron content of the alfalfa plants decreased, but there was no further decrease for additional lime. The average mean boron content for all treatments was 49.0, 41.1, and 41.7 p.p.m. respectively for the L, 2L, and 3L treatments. The fact that the boron content of the alfalfa decreased with the heavier rates of liming, even though yields also decreased, would seem to indicate that lime induced boron fixation in the soil. Midgley and Dunklee (9) showed that many different soils fixed boron when limed, the fixing capacities ranging from 20 to 85 per cent.

The average boron, calcium, and potassium contents of the alfalfa, in the first three cuttings on Rayne silt loam (No. 2), are presented in table 6. The calcium contents of the fertilized alfalfa were approximately equal for the 2L and 3L lime levels, but both were significantly higher than that for the L level. The potassium content of the fertilized alfalfa was also increased by the 2L and 3L treatments. The values obtained on the P-2K-B treatment were 1.84, 2.19, and 2.16 per cent potassium respectively for the L, 2L, and 3L treatments. Such an increase does not normally occur in healthy plants. The fact that the alfalfa was not growing in a normal manner at the high lime levels, as evidenced by overliming injury, may be responsible for the increase. Boron appeared to have had no significant effect on either the calcium or the potassium content of the plant tissue.

On Monongahela silt loam, a large increase in yield was also obtained at all lime levels from the use of phosphate and potash. On this soil an additional increase of approximately 7 per cent resulted from the use of borax. By analysis of variance this increase was found to be highly significant.

On Monongahela silt loam yields were not depressed by the high lime treatment. There was, however, evidence of overliming injury in the very young alfalfa seedlings, but it entirely disappeared before the first cutting was made. Why overliming injury did not occur to a greater extent is not clearly understood. As shown in table 2, the original chemical analysis is very similar to that of the Rayne soil (No. 2), and the same lime and fertilizer treatments were used on both soils.

The mean boron content of alfalfa grown on Monongahela silt loam with differ-



ent lime and fertilizer treatments is presented in table 7. Application of borax to this soil, as on the Rayne soil (No. 2), produced a greater than threefold increase in the boron content of alfalfa.

The boron content of the alfalfa that received no borax declined with added increments of lime. On the other hand, the alfalfa that received borax increased

TABLE 6

*Boron, calcium, and potassium content of alfalfa grown on Rayne silt loam (No. 2) and Monongahela silt loam with lime and fertilizer as variables*

TREATMENT*	PLANT ANALYSIS†					
	Rayne silt loam (No. 2)			Monongahela silt loam		
	B	Ca	K	B	Ca	K
	p.p.m.	per cent	per cent	p.p.m.	per cent	per cent
L	35	2.95	1.09	38	2.48	1.80
2L	..	....	....	20	2.61	1.74
3L	..	....	....	18	2.68	1.75
L-P-2K	27	2.21	1.67	23	2.15	2.11
2L-P-2K	16	2.53	2.09	14	2.24	1.98
3L-P-2K	20	2.67	2.00	13	2.23	2.13
L-P-2K-B	86	2.17	1.84	79	2.04	2.20
2L-P-2K-B	69	2.63	2.19	81	2.13	1.89
3L-P-2K-B	70	2.61	2.16	82	2.23	1.99

\* See footnote and pH values, table 5.

† Each value represents an average of three cuttings and three replications.

TABLE 7

*Mean boron content of alfalfa, in p.p.m. of dry matter, grown in pots on Monongahela silt loam with lime and fertilizer as variables\**

FERTILIZER TREATMENT†	LIME TREATMENT			FERTILIZER MEAN
	L (pH6.7)	2L (pH7.0)	3L (pH7.2)	
	p.p.m.B	p.p.m.B	p.p.m.B	p.p.m.B
None	33.3	20.6	19.3	24.4 ± .149
P-2K	22.3	16.0	13.6	17.3 ± .149
P-2K-B	75.6	78.6	77.6	77.3 ± .149
		(S. E. = ±.258)		
Lime Mean	43.7	38.4	36.9	
		(S. E. = ±.149)		

\* Each value represents the mean of five cuttings and three replicates.

† P = 200 pounds  $P_2O_5$  per acre; 2K = 250 pounds  $K_2O$  per acre; B = 20 pounds borax per acre.

in boron content when limed above pH 6.7 but began to decrease at pH 7.2. This would seem to indicate that fixation did occur in this soil but that it was less pronounced than in the Rayne soil and the plants were able to meet their requirements when borax was applied.

The alfalfa grown with phosphate and potash at the 2L and 3L lime levels con-



tained only 16.0 and 13.6 p.p.m. boron respectively. These plants, as pointed out earlier, were depressed in yield and showed marked boron-deficiency symptoms. Thus it is evident that boron at this level was too low for maximum growth.

Mild boron-deficiency symptoms were, at times, observed after the first cutting on the alfalfa grown without fertilizer at the 2L and 3L lime levels. Yields, however, were not depressed, and the boron content of this alfalfa averaged 20.6 and 19.3 p.p.m. respectively. It would appear that these plants were approaching a critical boron level.

The calcium and potassium contents of the alfalfa grown on Monongahela silt loam are given in table 6. The calcium content of the plants, like that of plants on the Rayne soil, was greater at the 2L and 3L lime levels than at the L lime level. The potassium content, however, in this case did not vary significantly with the lime applications. It was, of course, increased by the addition of potash. Boron again had no effect on the calcium or potassium content of the plant tissue.

The data in table 6 also show that the addition of fertilizer markedly decreased the calcium content of the alfalfa. This is especially significant at the high lime levels and may account, at least in part, for the fact that overliming injury was not prevalent on this soil. The calcium content of the alfalfa for these treatments was considerably lower than on the Rayne soil (No. 2) where overliming injury occurred.

#### CALCIUM-BORON RATIO OF ALFALFA

In the greenhouse study, the calcium-boron ratios for the alfalfa grown on the two samples of Rayne silt loam ranged from 210 to 2094. Boron-deficiency symptoms were observed on alfalfa when this ratio exceeded 1,245. On Monongahela silt loam the calcium-boron ratios ranged from 216 to 2125, and boron-deficiency symptoms appeared when the ratio reached or exceeded 1,255. In all cases when boron-deficiency symptoms appeared, the alfalfa plants contained approximately 19 p.p.m. boron or less.

The calcium-boron ratios on a number of alfalfa samples collected on several different soil types in West Virginia were also determined. These ratios ranged from 201 to 1,041. Of the 26 alfalfa samples analyzed, only four showed boron-deficiency symptoms. The calcium-boron ratios of these samples were 667, 944, 1041, and 923. The boron content averaged 18, 18, 17, 17 p.p.m. boron respectively. It will be noted that these ratios are much lower than those obtained from the alfalfa grown in pot cultures which also exhibited boron-deficiency symptoms. On the other hand, the total boron content of the alfalfa is very similar for the greenhouse and the field-grown plants. The wide differences in ratio were caused by the great variation in calcium content of the plants.

Thus it is evident that alfalfa on these soils has a well-defined critical boron requirement even at a wide range of calcium accumulation. It would appear, therefore, that the boron content of the plants is a more valuable criterion of predicting the need of boron fertilization than is the calcium-boron ratio. In this

experiment when the boron content of alfalfa tissue was 19 p.p.m. or less, a need for boron fertilization was indicated.

It is impossible within the limited confines of this study to predict when boron toxicity might be incurred. In the greenhouse study no detrimental effect was apparent when the calcium-boron ratio dropped to 210 or when the boron content reached as much as 90 p.p.m. The alfalfa obtained from farmers' fields was vigorous and healthy when the calcium-boron ratio was as low as 201 with a boron content of 128 p.p.m.

#### SUMMARY AND CONCLUSIONS

Soil samples from 13 counties in West Virginia, representing 23 soil types, were analyzed for available boron. The results indicated that the supply of available boron in the plow layer, in general, is sufficiently high to prevent serious boron deficiency in alfalfa. Only two samples were found to contain less than 0.30 p.p.m. boron. Many of the soils were found to contain boron within the range 0.30 to 0.35 p.p.m. The subsurface layer contained less available boron than the plow layer. Strongly leached soils of acid gray shale and sandstone origin were, in general, lowest in available boron and seemed most likely to benefit from boron fertilization. Cookport and Monongahela soils were most representative of this group. Frankstown, a strongly leached soil from limestone, was also low in available boron and may benefit from boron fertilization.

Biologically available boron in these soils was also determined. The method used was found to be of a limited value on West Virginia soils. Soil acidity, lack of fertility, and poor physical properties resulted in growth rates too slow for satisfactory analyses on many of the soils tested. It could only be concluded from this test that none of the soils appeared to be severely deficient in boron.

Alfalfa was grown in the greenhouse on two soil types, and a study was made of the yield response and chemical composition of the plants, as affected by boron treatments, when grown at varying known levels of calcium and potassium. The results are summarized as follows:

Applications of borax to Rayne silt loam did not significantly increase the yield of alfalfa hay at any of the lime or potash levels. When this soil was limed to pH 7.1 and higher, yields were markedly reduced, indicating overliming injury. Borax at 20 pounds per acre did not significantly reduce this injury. On Monongahela silt loam, the yield of alfalfa was increased approximately 7 per cent at all lime levels by the use of 20 pounds per acre of borax. Overliming injury did not reduce yields on this soil.

The boron content of the fertilized alfalfa plants, on both soil types, was increased approximately threefold by application of 20 pounds per acre of borax. Potash alone and potash and phosphate decreased the boron content of the alfalfa. This was probably caused by insufficient available boron in the soil to supply the additional boron needed for the increased yield which resulted from the two fertilizers. In general, the boron content of the alfalfa declined with added increments of lime. Soil fixation was indicated. From the data it was possible to establish a critical boron level in alfalfa at approximately 19 p.p.m.

The calcium content of the alfalfa plants increased with additions of lime to the soil. Additions of potash tended to increase the potassium content of the plants and to reduce the calcium content. Boron had no significant effect on either the calcium or the potassium content of the plant tissue.

Alfalfa plants which exhibited boron-deficiency symptoms were found to vary widely in the ratio of calcium to boron. The boron contents, however, were found to be very similar and the ratio differences to be caused by the great variation in calcium content of the plants. Thus it was concluded that alfalfa, on the soils studied, has a well-defined critical boron requirement even at a wide range of calcium accumulation and that the boron content of the plants is, therefore, a more valuable criterion of predicting the need of boron fertilization than is the calcium-boron ratio.

It was impossible within the limited confines of this study to predict when boron toxicity might be incurred. Alfalfa in the field was found to be vigorous and healthy, however, when the calcium-boron ration was as low as 201 with a boron content of 128 p.p.m.

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## STONY SOILS AND THEIR CLASSIFICATION

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In common language soil is called *stony*<sup>2</sup> if it contains a certain quantity of stones either scattered on the surface or imbedded in the earthy material. The stony part of such a soil may represent either outcrops of bedrock or detached fragments of rocks. The fragments may be residual, usually characterized by sharp edges and rough surface, or transported—more or less rounded and somewhat polished. The residual fragments usually increase in size, number, and freshness with depth, whereas the distribution of transported stones is rather erratic. Under certain conditions, however, the stones, residual and transported, accumulate on the surface as a result of removal of fine material by running water or wind. The most conspicuous accumulation of this kind is the "desert pavement."

There is no natural line of demarcation between the stony and earthy particles as regards size. Usually an arbitrary boundary between the stones and earth is placed between coarse sand and gravel, or in the vicinity of the 2-mm. diameter. The other criterion for differentiation between the sand and stones is petrographic. Generally, the individual grains of sand are represented by a crystal or a fragment of a single mineral, such as quartz, whereas even the smallest pebble or rough piece of grit is a mineralogical complex consisting of two or more different minerals. This, likewise, is not an absolute criterion—large pieces of quartz, feldspar, or any other mineral are graded solely according to size. The arbitrary boundary between the stones and sand at the 2 mm. diameter is largely technical. To the layman's mind the smallest stone, probably, should have at least, say, a half-inch diameter.

As regards stony land there is no upper limit of individual rocks. As regards the soil, however, such a limit must be recognized. Stones in a stony soil represent one of the mechanical fractions of its material. These fractions range from clay through silt, sand, grit, and gravel to the stones of a certain maximum size,

<sup>1</sup> Soil scientist, Division of Soil Survey. Some suggestions presented in this paper have not been accepted in current practice of the Division as formulated in reports of the committees on soil texture and on nomenclature and definitions of coarse fragments in soils. The major differences are indicated in the footnotes throughout the paper. It is hoped that these new suggestions may stimulate further discussion of the subject matter.

<sup>2</sup> According to the current practices of Soil Survey, the term *stony* is applied to soils "having angular rock fragments (excluding chert) over 3 inches in diameter; chert fragments over 10 inches in diameter; and thin flat sandstone, limestone, chert, slate and shale fragments over 15 inches on the longest axis" [Report of Committee on Nomenclature and Definitions of Coarse Fragments in Soils, July 1947 (mimeographed)], whereas soils having different stony material are called *cobbly*, *flaggy*, *gravelly*, *channery*, *cherty*, etc. The author now recommends that the term *stony* be applied to all soils that contain a certain quantity of stones of any kind, size, or shape, rather than only to soils having stones of some particular kind or size.

above which they no longer can be rightly considered as an ingredient of the soil. The concept of soil texture, or mechanical composition of the soil, should be broadened to cover the coarse or stony fractions, and classes such as stony loam, gravelly loam, and gritty loam should be treated on a par with sandy loam, silt loam, and clay loam.

One must discriminate somehow between stony land and stony soil. The land might be strewn with large boulders, some of which may be several tens of feet in diameter and weight, say, a hundred tons. Again, the land might be thick with outcropping ledges of bedrock. Obviously, neither bedrock and its outcrops nor large boulders belong to the soil proper. They characterize a stony land. The soil over the solid bedrock, no matter how thin it may be, or between the protruding ledges of bedrock or scattered boulders might be stony if it, itself, contains some coarse material, or it might be stone-free. Conversely, all areas covered with stony soil may be called *stony land*, but just as every herring is a fish but not every fish is a herring—so, not every stony land area is covered with stony soil.

The upper limit of the size of stones that can be considered as a component of the soil is no less arbitrary than the lower. Being a part of the soil material, the stones must be imbedded in the earthy matrix and not merely lie on the surface or protrude through the soil. Imbedding in the matrix refers especially to the A and B horizons, the combined thickness of which averages, probably, about 2 feet. This may suggest some idea about maximum size of stones that may be said to be imbedded in the soil. These stones hardly can be more than 1 foot in diameter, and even this size should be regarded as maximum, with average size not exceeding, say, 6 or 7 inches. Larger stones, whether fragments or boulders, might be numerous in some places, but their presence should not influence the definition of *stony soil*.

The next question is: How many stones must the soil have to be called *stony*? A few pebbles here and there hardly are enough to qualify the soil as *gravelly*. On the other hand, sediments consisting largely of cobblestones with a small amount of interstitial fine material hardly can be referred to as *soil*. Obviously, there ought to be certain limits of stone content in true *stony soil*. The soil may contain up to 40 per cent of silt or 40 per cent of sand without being considered either silty or sandy. Similarly, neither a small amount of gravel nor a few stones will make the soil gravelly or stony.

Furthermore, having established the tentative upper and lower limits of stoniness, one is faced with the problem of dividing the entire range into several grades, such as stony, moderately stony, or very stony, and setting arbitrary boundaries between them. Of necessity, all decisions or recommendations dealing with these problems are tentative and subject to changes according to the purposes of classification. Realization of certain facts and underlying principles may help, however, in arriving at a reasonably sound, however arbitrary, conclusion.

One of the things to be considered in dealing with stony soils is that the larger the individual stones, the more conspicuous they become. For example, 5 per



cent by volume<sup>3</sup> of gravel in the soil may not make this soil particularly "gravelly," but how will the soil look if 5 per cent of it by volume consists of larger stones? Consider an area 10 by 10 feet. Suppose that it has only one boulder measuring a foot in diameter. If such boulders are scattered through the field uniformly, then there are about 450 of them per acre in the first foot of the soil. The average distance between the stones is 9 feet. At a distance of 9 feet from each stone there are four other similar boulders, and at a distance of about 14 feet another four. Suppose also that the same quantity of stones is in the second and third feet of the soil. For all practical purposes the soil is rather stony, but all these stones amount to a little more than a 0.5 per cent by volume of the soil. Now, suppose that the soil contains about eight times as many stones or, say, between three and four thousands per acre in the first foot, which would make the stoniness equal to 5 per cent. Suppose further that the average diameter of stones is not 1 foot but only 6 inches, which would require another increase of about eightfold in number to make the same 5 per cent by volume. Hardly anyone would hesitate to define such a soil as *stony*.

On the other hand, consider a soil containing 5 per cent of grit. In all likelihood such a soil will not be called *gritty* but may be described as, say, sandy or loamy with an admixture of grit, or it may be said to be *somewhat gritty*.

This should illustrate the point that no uniform limits of stoniness or boundaries between the grades can be set for all fractions or size-groups of the stony material. The tentative grouping of stony soils and the taxonomic boundaries between these groups are presented in table 1. The figures showing percentages of stony material are neither absolute nor final. Their purpose is merely to convey the general idea. In arriving at them, the author tried to visualize a certain volume of the soil—sometimes a cubic foot, sometimes 100 or more cubic feet, either in the form of a foot-deep sheet over an area of 100 square feet or in the form of a cube having the depth of the average soil—and the effects which a certain amount of various stones could have upon the soil profile.

The table itself is by no means a classification of stony soils. Its purpose is to arrange systematically and to define certain possible groups of stony soils on the basis of their stoniness. Reasons for their differentiation, definitions, and discussions of the principles of their classification within the broad scheme of general soil classification are presented in the following parts of this paper.

#### DEFINITIONS AND DISCUSSION

##### *Grit*

*Grit* is a coarse, rough residue of decayed rocks, especially of coarse-grained rocks such as granite. Fragments of grit usually are rather crumbly and less

<sup>3</sup> Usually the quantity of stones in the soil is given in percentage by volume. As the average specific gravity of stones does not differ greatly from that of sand and silt, the percentage of stones by volume should be roughly of the same order as that by weight. The porosity of stones, however, is virtually 0, whereas that of the fine material is about 40 to 50 per cent. Hence, the percentage of stones by volume should amount to about 1.4 to 1.5 this percentage of fine material calculated on the same basis, that is, the volume of the solid.

TABLE 1  
*Tentative grouping of stony soils\**

CLASS	GROUP	GROUP SYMBOL	GRIT	GRAVEL	STONES
			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
O. Stone-free soils	—	O-00	0	0	0
A. Soils with in- closure of coarse material.....	Slightly gritty	A-01	<10		
	Slightly gravelly	A-02	.....	<5	
	Slightly cobbly	A-03	.....	.....	<1
	Slightly rubbly	A-04	.....	.....	<1
	Moderately gritty	B-11	10-20		
	Moderately gravelly	B-12	.....	5-10	
	Moderately cobbly	B-13	.....	.....	1-5
	Moderately rubbly	B-14	.....	.....	1-5
	(Medium)† gritty	B-21	20-40		
	(Medium)† gravelly	B-22	.....	10-20	
	(Medium)† cobbly	B-23	.....	.....	5-10
	(Medium)† rubbly	B-24	.....	.....	5-10
	Very gritty	B-31	40-75		
	Very gravelly	B-32	.....	20-50	
	Very cobbly	B-33	.....	.....	10-25
	Very rubbly	B-34	.....	.....	10-25
C. Stones.....	Imbedded‡ grit	C-11	>75		
	Imbedded‡ gravel	C-12	.....	>50	>25
	Imbedded‡ cobblestones	C-13	.....	.....	>25
	Imbedded‡ rubble	C-14	.....	.....	>25
	Free grit	C-21	100		
	Free gravel	C-22	.....	100	
	Free cobblestones	C-23	.....	.....	100
	Crushed rock	C-24	.....	.....	100
D. Rock-soled or shod soils developed from regoliths ranging in thick- ness from about 6 inches to about 10 feet but includ- ing patches of deeper soil	Any of the groups above. The same symbols with the letter underlined, as <u>A-02</u> ; <u>B-22</u> ; <u>C-14</u> .	X-XX			
R. Rock outcrops	Bare rocks including patches covered with regolith up to 6 inches thick.	R-			

\* Percentages are by volume and are subject to revision.

† Modifier "medium" may be omitted.

‡ The word "imbedded" simply indicates that the voids between the stones are filled or partly filled with some fine material such as sand or clay, whereas in "free" stones the voids are largely empty.

than an inch in the longest axis. In residual soil and regolith, however, the grit may lie in large crumbly chunks still preserving the fabric of the original rock but falling apart under slight pressure. Some fine-grained crystalline rocks such as gneiss or schist may decay into a finely laminated grit. Usually the grit acquires a rather bright rusty brown or pink color, in which it differs from the fresh rock.

A *gritty soil* contains from about 10 per cent to about 75 per cent (by volume) of grit. A content of grit in any soil amounting to less than 10 per cent may be referred to as "admixture." The material consisting of more than 75 per cent of grit may be called "imbedded" grit; its matrix, amounting to less than 25 per cent of the whole, usually consists of brightly colored clay. The imbedded grit grades into the free grit, which usually lies in large crumbly chunks or slabs.

#### Gravel

*Gravel* is an assemblage of rounded, smoothly surfaced, water-worn pebbles ranging in size from less than an inch to about 3 inches. Theoretically, the lower size limit of gravel is 2 mm.; as commonly referred to, however, it is but little less than half an inch. Both limits are entirely arbitrary. An individual piece of gravel is a *pebble*. All gravels are transported and erratic as regards the underlying bedrocks. Most gravel sediments are of a heterogeneous lithological composition and usually are more or less stratified.

A *gravelly soil* contains from about 5 per cent to about 50 per cent of gravel.<sup>4</sup> Content of gravel in any soil making up less than 5 per cent of the material may be referred to as an *admixture of scattered pebbles* or *occasional pockets of gravel*. The material consisting predominantly, that is, more than 50 per cent, of gravel may be called *imbedded gravel*, its matrix formed by any material from clay to coarse sand.

#### Cobblestones

*Cobblestones*, or cobbles, are rounded, smooth-surfaced transported stones ranging in diameter from about 3 inches to about 10 inches. Commonly the term *cobblestone* is applied to "naturally rounded stones larger than a pebble, especially one a few inches in diameter such as is sometimes used for paving streets" (Webster). The upper size limit of a pebble has not been agreed upon, but this description suggests that cobblestones generally would range in diameter from hardly

<sup>4</sup> The term *gravelly soil* as currently used in Soil Survey applies to the soils "having rounded, semirounded or angular fragments (not flat), other than chert; ranging in size from 2 mm. to 3 inches in diameter" (Report of Committee on Nomenclature and Definitions). It will be noted that the author suggests restriction of the term *gravel* to the assemblage of rounded, water-worn pebbles, which would conform more closely to the definition of *gravel* by Webster, and proposes the terms *grit* and *rubble* for the rough angular fragments of rocks (see definitions of *grit* and *rubble*).

As regards the amount of gravel in a *gravelly soil* the Committee on Soil Texture suggests tentatively about 20 per cent for the lower limit and about 70 per cent for the upper. In the author's opinion, both these limits, especially the lower one, may need to be lowered.

less than 4 or 5 inches to about 10 inches, the larger stones being called *boulders*. All cobblestones are transported.

A *cobbly soil* contains from about 1 per cent to about 25 per cent by volume of cobblestones and boulders. The content of cobblestones amounting to less than 1 per cent of the whole soil may be referred to as an *inclusion of scattered cobblestones and occasional boulders*, whereas the material more than one-fourth of which consists of cobblestones may be treated as imbedded cobbles and boulders. Again, all limits of percentages are entirely arbitrary and, in case of cobbly soils, probably even more arbitrary than in the cases of gravelly and gritty soils. One must bear in mind that the relative degree of conspicuousness and significance in practical soil uses increases with the size of individual stones. As has been pointed out, 5 per cent by volume of gravel does not make the soil conspicuously gravelly and does not seriously interfere with its cultivation, whereas the same quantity of large cobblestones averaging, say, 6 inches in diameter would make a fairly stony soil because every 100 square feet of it would include roughly 50 such stones in the upper foot.

#### *Rubbles*

*Rubbles* are rough-surfaced, angular, usually sharp-edged fragments of rocks ranging in size from about an inch to about 6 or 8 inches ["rough stone as it comes from the quarry . . . rough broken stones . . . used in coarse masonry . . ." (Webster)]. Fragments of rock larger than rubbles will be called just *rock fragments* or *broken rock*, whereas fragments less than an inch in the longest axis are included with the grit. Most commonly rubbles are residual and rest in place of origin. Transportation of rubbles and larger rock fragments is due especially to the force of gravity. Transportation by ice or water eventually transforms rubbles into gravel and cobblestones.

A *rubbly soil* (see definition of *skeletal soil*)<sup>5</sup> contains about 1 to about 25 per cent of rubbles. Both these limits might be 5 to 10 per cent higher if the rubbly material consists of small fragments not exceeding, say, 3 or 4 inches. Content of rubbles amounting to less than 1 per cent (and less than 5 per cent in the case of very fine rubbles) may be referred to as an *admixture of rubbles*, whereas accumulations of rubbles in excess of 25 to 50 per cent (depending on the average size of fragments) may be referred to as *imbedded rubbles or rock fragments*.

#### *Soils with heterogeneous stony fraction*

The coarse material of many stony soils consists of stones of different size groups, and several subgroups can be differentiated on the basis of composition of

<sup>5</sup> The terms *channery*, *shaly*, *slaty*, and *cherty* are currently used in the Soil Survey in definitions of soils having flat fragments of sandstone, limestone, and schist (*channery soils*), shale (*shaly soils*), slate (*slaty soils*)—all ranging from 2 mm. to 6 inches on the longest axis—or angular fragments of chert less than 10 inches on the longest axis (*cherty soils*) (Report of Committee on Nomenclature and Definitions). The author believes that terms such as *cherty*, *shaly*, and *slaty* may be useful for designating the lithologic character of certain individual soils, which collectively may be referred to as *rubbly* or *coarse skeletal*, if the rock fragments are larger than an inch, and *gritty*, if the fragments are less than an inch in diameter.



this material. The most common combinations are those including gravel and cobblestones. Since virtually all grits and rubbles are residual or are transported for a relatively short distance, especially by the force of gravity, whereas gravel, cobblestones, and boulders are transported, mixtures of either gravel or cobblestones with either grit or rubbles are rather rare in nature. One such mixture results from the decay of less resistant pebbles in old gravel beds into the secondarily residual grit. The other is formed by the deposition of a thin sheet of gravel or cobbles over bedrock that subsequently decayed into grit or became reduced to rubble.

As regards the composition of the stony fraction, the groups of the gravelly and cobbly soils may be divided into the following six subgroups (percentages refer to the stony material alone):

*Gravelly soils* (groups A-02; B-12; B-22; B-32)

1. Gravel free from cobblestones
2. Gravel with admixture of cobblestones (not more than 10 per cent cobblestones)
3. Cobbly gravel (10 to 40 per cent cobblestones)

*Cobbly soils* (groups A-03; B-13; B-23; B-33)

4. Gravelly cobblestones (40 to 80 per cent cobblestones)
5. Cobblestones with an admixture of gravel (more than 80 per cent cobblestones)
6. Cobblestones free from gravel

Soils containing rubble and grit can be classified on the basis of the same percentages. No special names for the subgroups are proposed. Their symbols, however, can be differentiated by an addition of a small letter to the group symbol—*a*- for subgroups 1 and 6; *b*- for subgroups 2 and 5; *c*- for subgroups 3 and 4. Thus, B-12*b* would indicate a gravelly soil, the stony fraction of which includes no more than 10 per cent of cobblestones, whereas B-13*b* would indicate a cobbly soil, the stony fraction of which may include up to 20 per cent of gravel (on the basis of the stony fraction alone).

#### *Soil skeleton*

Some earlier treatises on soils suggested the stony part of the soil be called its *skeleton*. Later, another suggestion was to include in the skeleton all material consisting of the highly resistant minerals such as quartz, irrespective of the size of individual particles<sup>6</sup>. If this latter concept of *soil skeleton* is accepted, it may become useful to differentiate between the *fine skeleton*, including the unreactive silt and sand (mostly quartz), and the *coarse skeleton*, including all material coarser than sand. If this were the case, all soils except *organic* would be *skeletal*.

<sup>6</sup> According to Zakharov, "the term *soil skeleton* refers to the more or less coarse residue of lithosphere in the soil material which survived weathering and soil formation. It consists of fragments of rocks and minerals more than 1 mm. and according to other authors more than 3 mm. in diameter. Size, shape and lithological character of these fragments as well as the degree of their preservation permit one to judge as to the bedrock from which a given soil has been developed and the character and tendency of the soil-forming processes. . . . Subangular shapes of the fragments indicate their formation in place or transportation for a short distance only, whereas rounded shapes bear witness of their having been subject to abrasion by water and wind." (Zakharov, S. A. 1927 Achievements of Russian science in the field of soil morphology, Rpts. U.S.S.R. Delegates to the First Internatl. Cong. Soil Sci., pp. 35-36, Moscow.)



The term *skeletal soil*, however, has a rather specific meaning and is applied only to a certain group of stony soils.

#### *Skeletal soil*

As originally defined every stony soil was referred to as skeletal or possessing a coarse skeleton. Gradually, however, the term *skeletal soil* began to acquire a more specific connotation. To the best of the author's knowledge its precise definition never has been published. Its specification developed by common usage. First the gravelly soils and then the cobbly and bouldery were dropped from the group of soils which might have been called *skeletal*. Seemingly, a general tendency is to restrict the specific name *skeletal* to gritty and rubbly soils in which the coarse skeleton consists of residual fragments of the underlying bedrock, and the fine, earthy material or *the flesh* of which is the residual product of complete decomposition of the same rock. In other words, a *skeletal soil* is a *stony soil in which the stony part intimately relates to both the initial rock and the flesh*. Hence, every skeletal soil must be rather thin or shallow over the bedrock and usually does not contain any erratic transported stones such as pebbles, cobblestones, or boulders. In gravelly or cobbly soils, such as those developed from certain glacial tills or alluvial materials, the stones do not relate to either underlying rocks or the fine material. They may be regarded, therefore, as a foreign inclusion rather than the true skeleton.

#### *Rock-soled (shod) soil<sup>7</sup>*

A *rock-soled* soil is a soil developed from a thin regolith underlain by a solid, hard bedrock at a depth ranging from less than a foot to about 10 feet. In some places, however, the surface of bedrock is very uneven and the rocks are exposed in numerous outcrops scattered over the land. In such places the thickness of regolith may range, within a short distance, from 0 to considerably more than 10 feet. It may or may not be practical to separate these small areas of deep soils from the shallow. One must discriminate, therefore, between the theoretical concept of rock-soled soil and the mappable units of such soils. The latter, naturally include scattered patches of soil which does not correspond to the theoretical limitations.

A rock-soled soil may or may not be stony. It might be gritty, gravelly, cobbly, skeletal, or perfectly free of any coarse material. Hence, the name *stony* must not be applied to all rock-soled soils, no matter how close to the land surface is the surface of bedrock and how numerous are the outcrops of this bedrock. It may be appropriate to call the land a *stony land* or *rockland*, but the term *stony land* must not be confused with the term *stony soil*, because the soil of stony land may be stone-free.

<sup>7</sup> *Sole*—is defined by Webster as "the bottom or lower part of anything, or that on which anything rests; to furnish with a sole." This new term *rock-soled* is suggested instead of *thin* or *shallow* because the latter has been used rather loosely in descriptions of various other soils such as soils with thin sola. An alternative to the hyphenated term *rock-soled* could be a shorter term *shod soil*.

*Embryonic soil*

The concept of a rock-soled soil should not be carried *ad absurdum*. For all practical purposes, a certain minimum thickness of regolith ought to be recognized below which it no longer is sufficient for the development of the soil in its common sense. Theoretically, a mere film of loose material on the surface of hard rock, especially if it is covered by some moss and lichens and supports a few other plants, is a *soil*. Sometimes it is spoken of as a *primitive* or an *embryonic soil* with the implication that such is the beginning of the soil, which may grow as a result of progressive deconsolidation of the rock and slow increase in the thickness of regolith. Attempts are being made to estimate the length of time necessary to attain the thickness of a few inches, a foot, or a few feet. These attempts appear somewhat speculative. To begin with, the thin sheets of loose material on the surface of hard rock rarely are truly residual. In most cases, this material is deposited by running water or wind. It may accumulate, rest for a few years, and be on the move again, so that its thickness at any given time in no way represents a cumulative effect of decomposition of the rock *in situ* and cannot be referred to as the initial stage of the development of a residual soil.

The embryo of a residual soil does not originate in such a way. Formation of a residual soil, perhaps, always begins with a deep decay and deconsolidation of the bedrock which may extend to a depth of many feet. Usually, weathering of rock is conceived as a succession of stages such as physical disintegration, chemical decomposition, both presumably abiotic, and finally soil formation due to the capture of the regolith by the biological factors. This is not necessarily true. Disintegration and decomposition may take place simultaneously, and the organisms may be active in these processes from the very beginning. The product of such decay usually is a crumbly material which still retains the fabric of an original rock but gradually acquires a somewhat different color that indicates certain chemical changes in the constituent minerals. At some, and usually not very great, depth some minerals decompose more profoundly, whereas more resistant ones remain in original position hardly changed at all. Thus, differentiation of the genetic horizons begins and as soon as such a differentiation becomes evident the material may be justly called an *embryonic soil*. It is not a mere film or just a few inches of loose dirt on the surface of hard rock. Its depth may be equal to the depth of a fully developed soil. Commonly, however, such an embryonic soil is *rock-soled* in the sense of the foregoing definition. It differs from the other rock-soled soils in the absence of an abrupt boundary between the regolith and the underlying hard rock; in the young residual soil the effects of decay of the parent rock disappear rather gradually. Most of the embryonic soils are rather gritty, and many of them are skeletal, the content of coarse skeleton increasing with depth.

The more advanced stages of the development of an embryonic soil are marked especially by development of the B horizon, which becomes enriched in clay and acquires a distinct and usually rather bright color. Such a development suggests that an especially strong hydrolytic decomposition of certain minerals takes place particularly in this horizon rather than on the surface.

*Cryptogenic soils*

The concept of *embryonic soil* as defined does not apply to soils with weakly developed profiles or, as some soil students prefer to say, "an incipient horizon differentiation." The degree of morphological distinctiveness of various horizons has no general relation to the progress of soil development. Some soils which have hardly passed the embryonic stage are characterized by a conspicuous, strongly developed B horizon, whereas many other soils just as old and "mature" as any soil can be are hardly marked by any horizon differentiation. Some of the latter soils are difficult to distinguish from the fresh regoliths unmodified by any pedogenic processes such as leaching, differential hydrolysis, or accumulation of humus.

New regoliths, such as fresh alluvial or air-borne sediments, may become subject to modification by soil formation. Theoretically, they may be referred to as *soils* as soon as they are anchored and occupied by vegetation. Naturally, for a number of years, probably even several centuries, the profiles of such soils should remain rather monotonous and such soils may be called *embryonic*. The rate of development of these soils may or may not be similar to that of the embryonic residual soils, the difference being due to the difference in lithological composition of the parent materials. The transported sediments consist largely of previously weathered materials that have lost a certain part of, if not all, the less resistant minerals, the decomposition of which in a residual soil is one of the principal factors of a rather fast differentiation of the soil horizons. Assorting of the sediment may be so drastic that the soil derived from such a sediment may never acquire a profile even remotely resembling that of the residual soil even if both these soils develop in essentially similar environments. Presumably the same factor is responsible for the existence of "old" and "mature" soils with an exceedingly weak profile (for example, morainic sands under yellow-pine forest).

The development of a new soil from the fresh sediments presupposes the end of deposition of such sediments. A different type of formation represents the regoliths which are still in the process of accumulation, such as sediments of the flood plains, active alluvial fans, coastal beaches, and sand dunes. No cumulative effects of soil formation can be produced on these materials and no profile development can take place. In a sense, these regoliths cannot be referred to as *soils* as long as their deposition continues unless we would recognize a special group of perennially infantile soils.

Since the acquired or inherent characteristics are weakly developed, if at all, in any of the aforementioned soils, the precise identification of these soils is difficult and usually is based on circumstantial rather than direct evidence. The author proposes extension of the term *cryptogenic soils* to all soils characterized by an obscure or total lack of profile development. The heterogeneous group of cryptogenic soils (soils of "obscure or unknown origin") should include the perennially infantile soils, embryonic soils on fresh regoliths, old soils lacking sufficient horizon differentiation, probably because of their development from pedogenically sterile parent materials, and, perhaps, other similar surface formations.



The cryptogenic soils may be gritty, gravelly, stony, skeletal, or stone-free; they may be deep or rock-soled and may be subdivided into the corresponding groups on the basis of their composition. Whether any one of them is embryonic, perennially infantile, or lithologically sterile can be determined only by inference from circumstantial evidence.

#### PRINCIPLES OF CLASSIFICATION

The purpose of every classification is to arrange the objects or facts into a logical system showing various degrees of relationship, similarity, or difference among these objects. It has been emphasized from time to time that classifications are made especially to facilitate the remembrance of various things. This, perhaps, is an oversimplification of the purpose of classification. Mechanistic arrangements for mere convenience must not be allowed to overshadow the grouping based on natural relationships even if the latter would make it more difficult to remember the proper place of some individual objects.

There are two methods of classification: one begins from the top and develops downward, toward the primary individuals; the second develops in the opposite direction, that is, from the individuals upward. As regards soil classification, one may consider all soils of the world and divide them into a few very broad groups or kinds, then consider each of these kinds separately and divide them into smaller groups and these into still smaller and more specific groups until the level of indivisible individual types is reached. This is the method of soil classification largely employed by the Russian school of soil science.

The other method begins with the individual soil bodies and groups them into successively larger and more inclusive taxonomic units. This is the method largely employed by the American school.

Naturally, neither method can claim a monopoly, and for the purposes of an objective natural classification both are useful, and one should supplement the other.

The prerequisite of any classification is knowledge of the objects of classification sufficient for an understanding of the relationships among them and for correct interpretation of their similarities and differences. Without such knowledge, there can be no possibility of an objective classification; and if this knowledge exists, then one should know where and when to use either method or both.

Classification consists essentially of grouping objects at various levels of abstraction into progressively broader and more inclusive taxonomic units. The first task of classification is to establish appropriate criteria for each level of abstraction. In formulating these criteria one must bear in mind the method of classification to be followed. If one employs the first method he must *divide* larger units into successively smaller ones. The division must be based on significant selected *differences* between the objects or their homogeneous groups. *Hence, his criteria are always the differences between the objects in one or another respect which indicate the boundaries between the smaller units within the larger one that is subject to division.*

On the other hand, if the second method is used, then one must build up the

larger and more inclusive units by *grouping* the smaller ones on the basis of significant *similarities* of the objects. In this case the criterion is necessarily the *similarity or uniformity of the objects* to be grouped in one respect or another. Obviously, the principle of uniformity of the things to be grouped must apply to every level of abstraction throughout the system of classification, although the *respect* in which the object must be similar (or differ, if the first method is used) varies with the level of abstraction. For example, at one level, the objects may be similar as to color or general appearance of the soil; at another, to the kind of parent material; and at still another to, say, the texture of the surface soil.

Assumption of similarity in any given property as the criterion for grouping at a given level of abstraction implies that the objects so grouped may or may not be similar to one another in any other property, no matter how important it may be. For example, if the criterion of grouping soils is their uniformity in color throughout any single group, then the soils of each group may vary in texture, parent material, or any other property except color.

Employing both methods, one must build up larger units on the basis of certain similarities among the smaller units to be brought together and separate the synthetic large units from one another on the basis of significant common differences between the various groups of the smaller units. Such a procedure must rest on certain basic principles such as the following three:

#### *First principle*

The first principle of classification is the *principle of the wholeness of taxonomic categories*, which means that all individual things, bodies, or phenomena subject to classification, without exception, must be considered at any given level of abstraction from the top to the bottom of the system of classification. Any exception to this rule would leave a certain number or part of the objects unclassified at a given level of abstraction and, hence, preclude their being classified at all higher levels.

#### *Second principle*

The second principle of classification is the *principle of homogeneity of taxonomic categories*, which means that each category must consist of units of essentially the same taxonomic rank. Uniformity of taxonomic rank means that all units at a given level of abstraction must be based on a single criterion which should apply to the grouping of all individuals throughout this level of abstraction. It would be a violation of logic to place in a single category some unit based on one criterion and others based on a different criterion. If some particular criterion does not apply to all individuals, then it must be recognized that such a criterion does not belong to—and cannot be used at—a given level of abstraction. A single criterion should derive from a number of determining characteristics of the objects to be classified which serve as the sources of criteria.

Each criterion used at any level of abstraction must be the uniformity of the objects to be grouped in one respect or another. Therefore, formulation of every criterion must begin with the words “uniformity of the objects (that is, either individuals or units of the preceding lower category) as to . . .”



At the lowest level of abstraction the criterion must be uniformity of the objects in respect to all determining characteristics, without exception. At the next higher level of abstraction it must be uniformity of the units of the preceding category in respect to all determining characteristics except one (or a single group of mutually interrelated) characteristics. At the next still higher level, another characteristic must be eliminated from the sources of criteria, and so on to the highest level of abstraction, at which only the fundamental determining characteristic should serve as the source of criterion. A gradual elimination of the particular sources must be based on the following principle.

#### *Third principle*

The third principle of classification is *the principle of taxonomic ceiling of the determining characteristics*, which means that each determining characteristic of an object of classification has a certain ceiling above which it cannot serve as a source of the criterion for grouping these objects into the units of a higher taxonomic rank. The determining characteristics of the lowest ceiling must be dropped first, to be followed by the characteristics of the successively higher ceiling. At the highest level of abstraction only the determining characteristics having the highest taxonomic ceiling can serve as the source of criterion.

The taxonomic ceiling of any particular characteristic is determined by the relative importance of such a characteristic or its specific weight in determining the individuality of the unit and relationship of this unit to the other units of an equal taxonomic rank.

At the present level of our knowledge, a certain arbitrariness in evaluating determining characteristics as to their ceilings cannot be avoided. To a large degree, determining the relative importance of various characteristics depends upon the objectives of classification. For one objective a given characteristic may be considered rather unimportant and assigned a low ceiling of independence, whereas for other objectives the same characteristic may be fundamental and be given a much higher ceiling.

An example will illustrate the point. In classification of animals one may consider that possession of wings and ability to fly is an important determining characteristic on the basis of which all flying animals can be grouped together to be contrasted with, say, the walking and crawling animals. The criterion for building up such groups is the similarity of individual organisms as to the manner of mobility. Hence a mosquito, a crow, and a bat will be classed together. Then at some higher level of abstraction it will be found that one is an insect, the other a bird, and the third a mammal, the first being invertebrate and the others vertebrates. Being vertebrate or invertebrate is recognized as a broader and more nearly fundamental characteristic than the ability either to fly or to crawl. Hence all animals will be reclassified as vertebrate and invertebrate, each group including some flying, crawling, and walking individuals. In other words, at no level of abstraction will a single group including all flying, living beings be recognized. Hence it will be recognized that the taxonomic ceiling of the characteristic of ability to fly is lower than that of being an insect, a bird, or a mammal.

Similarly with soils, being a stony or stone-free soil is an important characteristic, on the basis of which all soils can be divided into two or more broad groups such as stone-free, gravelly, and stony. Then it will be found that there are stony podzols, stony chernozems, and stony laterites. Now, being a podzol, chernozem, or lateritic soil will be recognized as a more important characteristic than being stony or stone-free, and all soils will be classified as podzols, chernozems, etc., each of these groups including some stony and some stone-free individuals so that at no level of abstraction will all stony soils form a single taxonomic unit. Thus, it will be recognized that the taxonomic ceiling of the criterion based on mechanical composition of the soil material is lower than that of the criterion based on the mode of formation of the soil. In other words, at a certain level of abstraction the mechanical composition of the soil might serve as a criterion for classification of soils, whereas at some higher level which is above its taxonomic ceiling this characteristic will be engulfed by the other having a higher ceiling.

If, however, one is classifying soil for some technical or engineering objectives then he may consider that mechanical composition is the most important characteristic, whereas being a podzol or chernozem is of relatively minor significance. In view of such specific objective of classification the mechanical composition of the soil may be given a higher ceiling than that of the mode of formation.

#### CLASSIFICATION OF STONY SOILS

The first problem in classifying stony soils is to determine the taxonomic ceiling of stoniness. As has been said, the stony part of the soil material is a coarse mechanical fraction of this material. Hence, large groups or classes of gritty, gravelly, cobbly, and skeletal soils should be treated on a par with sandy, silty, clayey, and various other textural groups.

The textural classes, however, are not incorporated into the natural soil classification. They are somewhat similar to the groups of flying, swimming, crawling, and walking animals, which likewise are not accepted in classification of animals. Each textural class including the class of stony soils is distributed among various groups which are built on the basis of other criteria so that the independent taxonomic units of various stony soils do not appear in any higher category of classification. Therefore one must conclude that the taxonomic ceiling of stoniness is rather low.

Differentiation of the soil on the basis of texture is applied to identification of the individual soil types within a single soil series. The generally accepted criterion for building up a soil series is the uniformity of the soil types in all determining characteristics except for the texture of the uppermost part of the profile. In this case textural differences refer specifically to the "surface soil" or the upper one or more horizons. The texture of the deeper soil horizons and especially of the parent material cannot vary widely within a single soil series.

Stoniness of a stony soil, however, refers to the composition of the entire soil profile including the parent material. In fact, stoniness or coarse skeleton is a characteristic of the parent material itself, whereas variations in the texture of

the A horizon within a soil series may be due to modification of the original texture of the parent material by soil formation.

Character of the parent material is one of the principal determining characteristics of the soil series, which implies that several soil types may develop from essentially the same parent material. Hence, the taxonomic ceiling of stoniness, which is one of the determining characteristics of the parent material, cannot be lower than the level of the soil series; in fact, it must be somewhat higher than this level. Units of stoniness which are included in table 1 are not differentiated on the basis of lithological character of the stony material. A gritty or a skeletal soil must contain a certain amount of grit or fragments of rock respectively. The grit may derive from various rocks such as granite, diorite, schist, or basalt. The coarse skeleton may consist of fragments of granite, limestone, sandstone, lava, basalt, gneiss, flint, chert, or any other rock. All soils in any of these groups are gritty or skeletal (rubbly) and may fall into a corresponding textural group, but each of them individually represents a different soil series because of the lithological differences in parent materials. If several such soils develop side by side in a similar environment as to climate, topography, drainage, and vegetation then they may acquire a fairly uniform morphological profile and can differ from one another mainly in the lithology of their skeletons.

Whether the soil series represented by these soils should or could be grouped together to form an independent taxonomic unit composed entirely of similar stony soils cannot be decided at present because the criterion for such a grouping has not yet been found. It appears, however, that eventually soil series will be grouped into soil families at the next higher level of abstraction. It is probable that the criterion for such a grouping will be the uniformity of the soil series in all respects except parent material.

This does not mean that any single family will include the soils derived from an extremely wide a range of parent materials, because some materials might differ from one another so much that the development of morphologically similar soils from them is impossible. For example, it is not probable that the soils developed from a calcareous till and from morainic sand would acquire profiles that are sufficiently similar to warrant placing these soils into a single group at a relatively low level of abstraction. On the other hand, it seems quite probable that soils developed from various sands or clays of different origin might acquire, under given conditions, a fairly uniform general character. This suggests a possibility of emphasizing and using the taxonomic significance of the texture of the entire soil and its parent material, not merely of the surface soil. Such families would consist of morphologically and genetically similar soils developed from certain textural groups of parent materials such as sands, loams, clays, stony clays, or gravelly sands.

These groups would not be so large as the textural classes because their size would be controlled by the acquired characteristics superimposed upon these materials so that the soils developed from essentially the same parent material but different as to their profile would belong to different families.

If the concept of a soil family is based on these lines, then the existence of

independent families of gritty, gravelly, stony, or skeletal soils will be recognized, and consequently the taxonomic ceiling of stoniness will be raised to the family level.

It is possible, however, that the concept of a soil family will be built on a broader basis. For example, the criterion for grouping soils into a single family may be uniformity of the soil series in all determining characteristics except those that are inherited from the parent materials. In this case the taxonomic ceiling of all inherited characteristics including stoniness will be below the soil family level, and no independent soil families of any stony soils will be recognized because the presence or absence of the coarse skeleton in any soil is always an inherited feature.

Whether the soil family is a narrow or rather broad group, the taxonomic ceiling of stoniness is either at or below the level of the family. Any grouping of soil families at any higher level of abstraction represents such broad and inclusive taxonomic units that formulation of criteria for their differentiation is no longer feasible without employment of the broad genetic factors and disregard for the individual characteristics of the lower taxonomic units. Consequently, these criteria must be based entirely on the high ceiling determining characteristics such as the general type of weathering and the mode of soil formation controlled by the general physiographic environment. Hence, there is no room among these higher groups for any independent and equally ranked groups of stony soils.

Soil systematics recognizes numerous individual types of gritty, gravelly, cobbly, and skeletal soils. These are grouped into the independent series of gritty, gravelly, cobbly, and skeletal soils. Depending upon the definition of the soil family, these soil series may or may not be segregated into independent families of such soils, but this is the limit. At the higher level of abstraction, independent families of skeletal podzolic soils and gravelly podzolic soils must unite with the families of the stone-free podzolic soils—both of which may be either deep or rock-soled, strongly developed or weakly developed—to form such broad groups as those of the gray-brown podzolic or red-yellow podzolic soils.

#### NOTE ON NOMENCLATURE

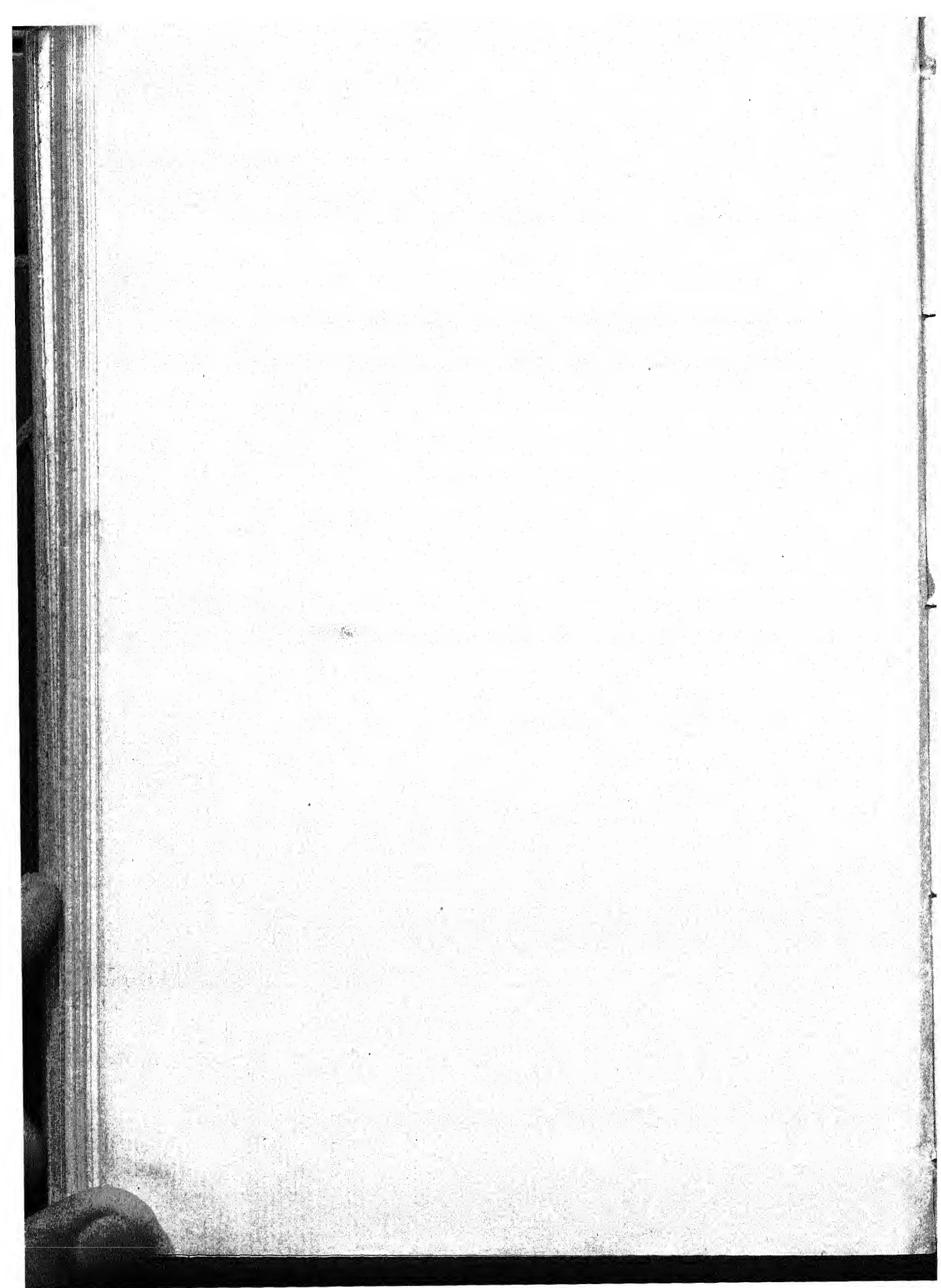
According to the American system, the name of a soil type is a combination of a certain geographical name, which is the name of the entire series, and the texture class name, which represents the texture of the upper horizon, or, as generally understood, the topsoil. Not a few soil types, however, bear such names as *so-and-so gravelly sand* or *so-and-so stony silt loam*. These and similar names are not entirely consistent with the general principle. The words *sand* and *silt loam* refer exclusively to the texture of the surface soil. The parent material of the silt loam type may be clay or clay loam, and its B horizon in many cases is clay. The subsoil of the sandy type may consist of loamy sand or sandy clay. A gravelly or stony type, however, although named on the basis of the surface soil is usually, although not always, gravelly or stony in the entire soil profile because of the character of the parent material. Hence,



*gravelly* and *stony* in the soil type name have a broader connotation than *sand* and *silt loam*. The former describe not an individual property of a given type but a characteristic which should be the property of the entire soil series. A few soil series do include stony and stone-free types, since stones are present only in the surface soil of some and in the parent material of all. With some exceptions, therefore, words like *gravelly*, *gritty*, *stony* do not enter the definition of the individual soil types apart from the series because they are a part of the definition of the series as a whole.

The name of the series, however, is merely a geographical name which does not itself connote any particular characteristic of the soil itself such as color, composition of the parent material, or mode of formation. The name of a series covers all individual properties of the given series, and since each series has a different name there is no need to attach any modifier to these names. The name of a given series should call to the mind of a person familiar with these soils whether the series consists of gravelly, skeletal, or stone-free soils; black, brown, or red soils; calcareous or acids; and so on.





# SOILS DEVELOPED FROM BASALT IN WESTERN COLORADO

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The relation of soil characteristics to differences in vegetation and climate with increasing altitude in western United States has been studied by Harradine, by Storie, and by Thorp.<sup>1</sup> Their studies dealt with soils developed from a variety of parent materials. These and other studies have indicated that within a given climatic-vegetal zone the lithology and structure of parent rocks exerts a major influence on soil development. Martin and Fletcher<sup>2</sup> reported on soils developed essentially from one type of gneiss in Arizona. Their study extended from the desert at 3,000 feet to the fir-spruce zone at about 10,000 feet. Powers<sup>3</sup> reported a study of soils developed primarily from loess, but his study terminated at 5,000 feet in the Ponderosa-pine-Douglas-fir zone.

The characteristics of soils developed from one type of parent material, basalt, under successive climatic-vegetal zones from the desert to the high spruce forest are the subject of this study in western Colorado.

## SITE CONDITIONS

The Grand Mesa of Colorado, a typical small plateau, is located well west of the main chain of the Rockies between the converging arms of the Gunnison and Colorado Rivers. From an approximate elevation of 10,800 feet at the east end, its smooth surface drops to 10,000 feet at the west end, a distance of 14 miles. It is surrounded by vertical cliffs 300 to 400 feet high. Within a distance of 6 miles from the west end of the mesa, elevations drop to below 5,000 feet in the Grand Valley.

The mesa top, formed by a series of thick basaltic flows of late Tertiary time, overlies soft Tertiary and Cretaceous sediments more than 5,000 feet thick. Subsequent to the lava flows down ancient valleys, the drainage pattern reversed itself by eroding away the shale uplands on the valley sides and then cutting deep valleys in the soft shales, leaving the hard basalt in a superior position as the protecting cap of the mesa (fig. 1). The east part of the mesa was exten-

<sup>1</sup> HARRADINE, F. Relationship between soils, topography, vegetation, and land use across the Northern Sacramento Valley of California. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 356-359. 1946.

STORIE, R. E. Relationship between topography, vegetation, and soils in Northeastern California. *Soil Sci. Soc. Amer. Proc.* (1937) 2: 567-570. 1938.

THORP, J. The effects of vegetation and climate upon soil profiles in Northern and Northwestern Wyoming. *Soil Sci.* 32: 283-302. 1931.

<sup>2</sup> MARTIN, W. P., AND FLETCHER, J. E. Vertical zonation of great soil groups on Mt. Graham, Arizona, as correlated with climate, vegetation, and profile characteristics. Univ. Ariz. Tech. Bul. 99. 1943.

<sup>3</sup> POWERS, W. L. Vertical zonation in the Umatilla area, Oregon. Paper presented before Western Society of Soil Science, 1940. Processed.

sively glaciated by three major ice advances, the two earlier advances depositing till fields. These fields are referred to as old and the new till in this paper. The glacial deposits have resulted in important soil differences. Pleistocene waters carried huge quantities of basalt cobbles (referred to as basalt drift) from the rim down over the slopes and into the Grand Valley to be deposited as alluvial fans over the shales. Thus, the same basaltic rock is the dominant soil parent material from the desert to the spruce zone. During this glacial depositional process, shale and basalt alluvium mixed in some places. This necessitated care in selecting study sites in steeper parts of the area.

The sand fractions from soils on the mesa top were examined. Such minerals as mica, hornblend, quartz, limonite, magnetite, and opal (variety hyalite?)

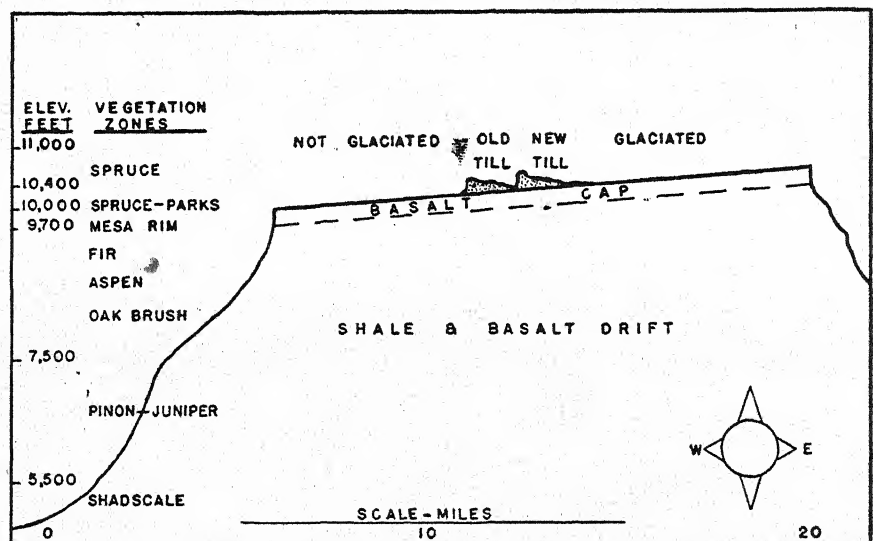


FIG. 1. SKETCH OF GRAND MESA AND ADJACENT SLOPES SHOWING VEGETATION ZONES IN RELATION TO ELEVATION, TOPOGRAPHY, AND GEOLOGIC CONSTRUCTION

were observed. The sands were very fine and ranged from sharply angular to subangular. There was no apparent significant change in composition of the sand from the surface to the deeper subsoil layers. Volcanic ash did not appear to be present. It was not possible to obtain a mineralogical analysis of the fresh basalt. The presence of the very fine quartz grains suggests some wind-deposited material, but from the position of the mesa and the behavior of the snow due to wind drifting it seems doubtful that wind-deposited dust has been greater on the mesa than can reasonably be expected for nearly all land surfaces of the earth. Because of the large quantities of basalt gravels and stones throughout the solum and scattered over the surface, it seems reasonable to assume that the soils of this study owe their characteristics to the basaltic influence insofar as parent materials are concerned.

The mesa is snow-covered from September to June. Summer showers are

light. Total annual precipitation is estimated to be 30 to 35 inches on the west end of the mesa but is considerably greater above 10,400 feet. Precipitation decreases only slightly beneath the rim in the aspen and upper oak-brush zones, but drops to about 8 inches in the valley. Summer thunderstorms are frequent below the rim. Summer temperatures are always low on the mesa, but rise to a July average of 78°F. in the valley, where temperatures of 105°F. are not uncommon.

Climatic differences are strongly reflected in the banding of vegetation types. Shadscale (*Atriplex confertifolia*) and associated plants occupy the lower zone and are indicative of its droughty, desert nature. At about 5,500 feet the pinon-juniper (*Pinus edulis-Juniperus utahensis*) zone comes in and extends upward to the oak brush (*Quercus gambelii*) zone at about 7,500 feet. Aspen (*Populus tremuloides*) and Douglas fir (*Pseudotsuga taxifolia*) in scattered patches replace the oak brush under the rim. The boundaries between vegetal zones are irregular. Because of differences in site conditions, they vary as much as several hundred feet in elevation locally. The westward extension of the mesa is dominantly grass parks with scattered patches of spruce (*Picea engelmannii*). East of an elevation of about 10,400 feet, spruce occupies all of the mesa except the wet sedge meadows. Huckelberry (*Vaccinium* sp.), an indicator of acid soils, grows extensively under the spruce in this eastern belt. The vegetal aspects and the type of terrain of the area studied are shown in figure 2.

#### SOILS

Soils with distinctly different characteristics have developed in each vegetational climatic zone (table 1). Since the parent materials are the same, profile differences can be attributed to other soil-forming factors. Except for the wet meadows on the mesa, drainage is good for all soils. Profile characteristics indicate that most soils are mature. Comparisons between soils are based on the solum arrangement, thickness of horizons, color, texture, structure, organic matter, and reaction.

##### *Solum arrangement*

With few exceptions, all profiles from the desert to the mesa top have prominent A, B, and C horizons. B horizons are sharply distinguished by color, structure, and texture from the A and C horizons. Soils developed from new till are azonal in character without distinct B horizons, whereas those developed in the glaciated area from bedrock above 10,400 feet are heterogeneous in this respect. Only the soils in the desert have a thin, vesicular surface crust. Soils developed under grass in the mesa parks have an A<sub>3</sub> horizon differing sharply in color from the A<sub>1</sub> and B layers (fig. 3A). An A<sub>2</sub> horizon indicating podzolization is sometimes encountered under spruce but only above 10,400 feet.

##### *Horizon thickness*

The thickness of surface horizons increases in each successive zone from the shadscale to the mesa parks (table 1). The surface crust of the soil in the desert



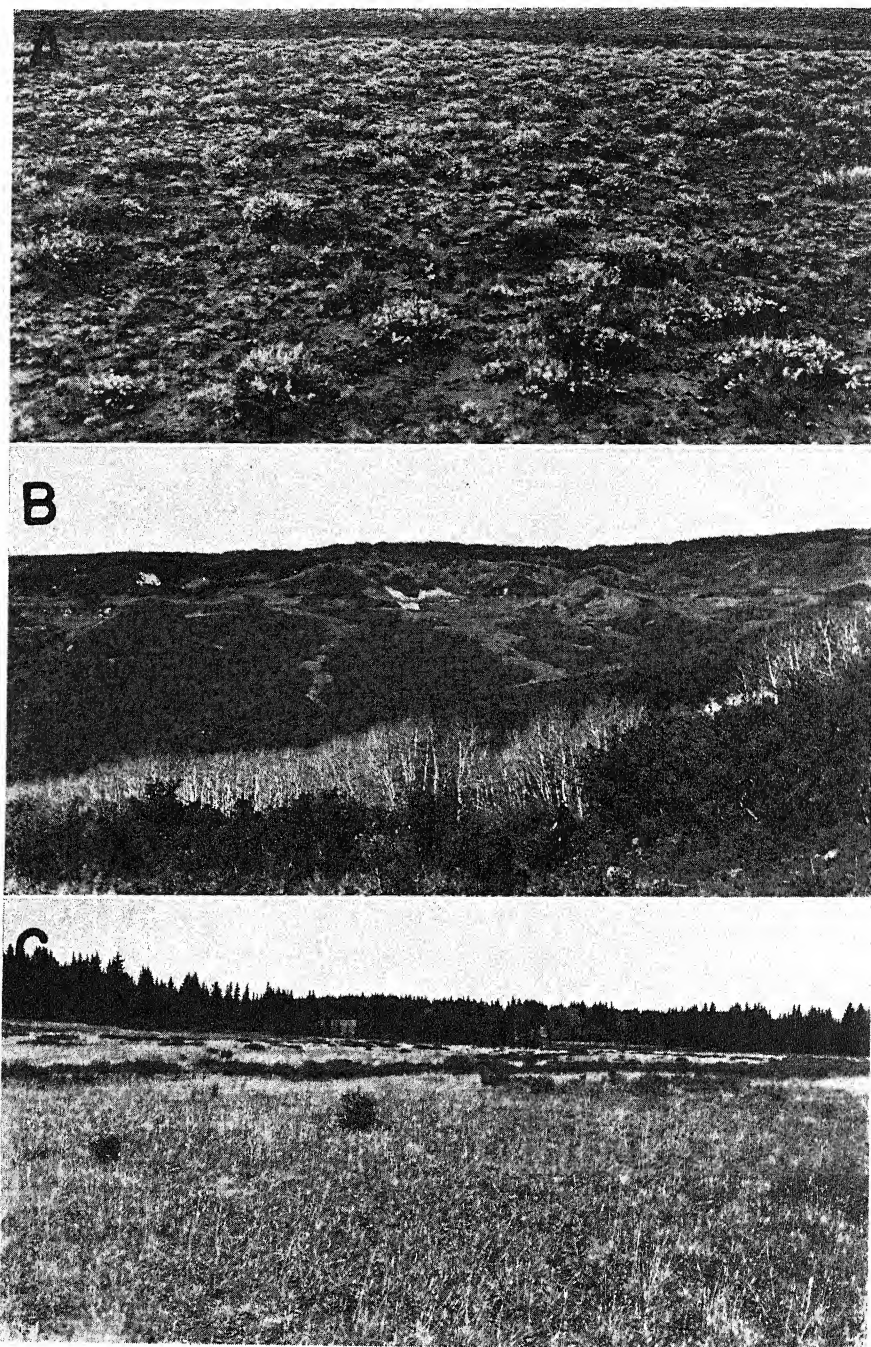


FIG. 2. GENERAL ASPECTS OF VEGETATION AND SITE CHARACTERISTICS OF THE GRAND MESA  
A—Smooth-surfaced ancient alluvial fans of the shadscale zone; B—steep slopes and dense cover of oak brush, aspen (light-colored belts), and fir (dark patches) beneath the mesa rim; C—level terrain and typical pattern of grass parks and spruce on mesa top.



TABLE 1

Some characteristics of soils from basalt in different vegetation zones from desert shadscale to high altitude spruce forest\*

VEGETATION ZONE	HORIZON	HORIZON THICK-NESS, COMMON RANGE	COLORS†		ORGANIC MATTER	pH‡
			Value	Color		
Shadscale ( <i>Atriplex confertifolia</i> ) (Desert)		inches			per cent	
	A	1-6	5YR 5/4 6/4	rB,lrB	1.3	8.2
	B	8-10	5YR 7/2	pG		8.2
Pinon-Juniper ( <i>Pinus edulis-Juniperus</i> sp.) (Under mesa rim)	C					7.7
	A	5-7	10YR 4/2	gB	2.6	7.9
	B	8-12	2.5YR 3/2	d r B		7.3
Oak Brush ( <i>Quercus gambelii</i> ) (Under mesa rim)	C		7.5YR 7/2	p G		8.0
	A	9-14	5YR 3/1 4/1	v d G, d G	4.0	7.2
	B	15-20	5YR 4/4 4/6	r, y R		6.8
Grass Parks (On mesa) Basalt bedrock	A	18-26	5YR 3/2 2/2	d r B	6.1	6.5
	B	16+§	5YR 4/4 4/6	rB, yR		6.6
Old till	A	18-25	5YR 4/3 4/4	rB	4.4	6.4
	B	40+	10YR 6/4	l y B		6.6
New till	A	14-18	10YR 5/2 5/3	g B, B	4.5	6.5
	B	16+	10YR 5/3 6/4	B, l B		6.6
Spruce ( <i>Picea engelmannii</i> ) (On mesa) Basalt bedrock	A	10-18	7.5YR 8/6	r Y	3.4	5.9
	B	34+	5YR 5/4	r B		6.9
	C		2.5 Y 4/2	g B		6.8
Old till	A	12-16	5YR 3/4	d r B	4.0	—
	B	14+	7.5YR 6/6 5/6	y R		
New till	A	12-14	5YR 4/3 4/8	r B, y R	5.6	—
	B	18+	5YR 5/6	y R		
Wet Meadows	A	10-18	10YR 3/1 3/2	v d G, vdB	7.7	6.7
	C		7.5YR 5/6	yR		

\* All data are the results of measurements on two or more profiles. Since the data all checked very closely, only the means are reported.

† All color values and names according to the Provisional Soil Survey Color Names 1947 of the U. S. Department of Agriculture, Division of Soil Survey. These color coordinates are in terms of the Munsell hue, value, and chroma. All colors are for dry soil. B—brown, G—gray, R—red, Y—yellow, l—light, d—dark, v—very, y—yellowish, r—reddish, g—grayish, p—pinkish.

‡ Glass electrode.

§ Actual thickness not determined but is greater than the figure shown.

is usually less than 1 inch thick, but the A horizon is 6 inches thick in many places. The maximum thickness in the pinon-juniper zone is 7 inches, but it occurs in many places. In the oak brush, more irregularity occurs in the surface soil, but 10 inches is a good average thickness. On top of the mesa, soils developed under spruce range in thickness of surface from 10 to 18 inches but 12 inches is the common depth. In grass parks the common thickness is 16 inches, but the range is from 14 to 26 inches. In these last two cases it appears that

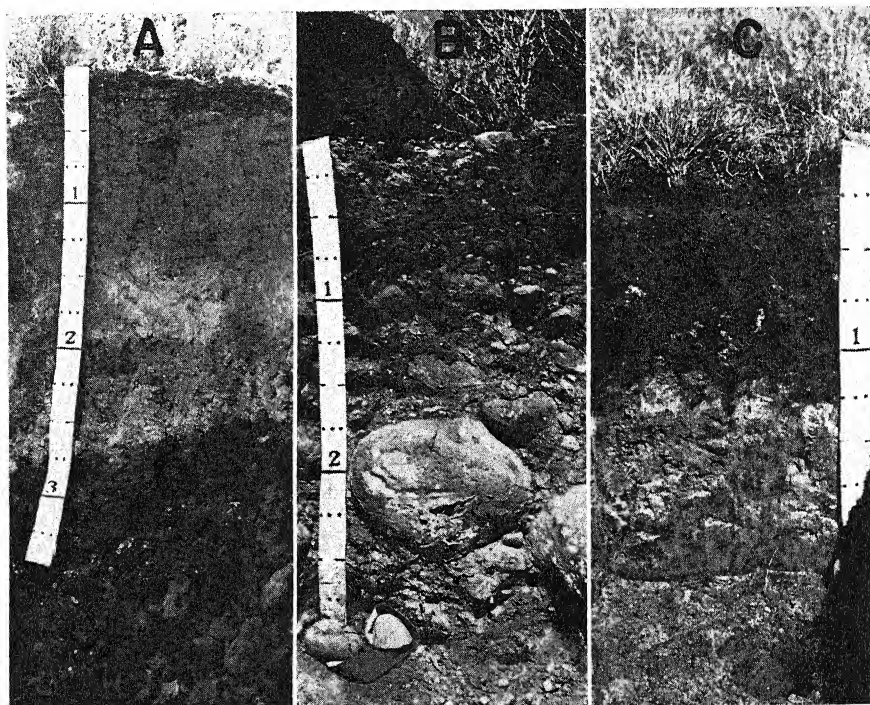


FIG. 3. TYPICAL PROFILES DEVELOPED FROM BASALT

A—From bedrock in grass parks on mesa top, showing dense claypan subsoil overlain by light colored  $A_3$  horizon; B—from basalt drift in lower part of oak brush zone; C—from bedrock in wet meadows on mesa top.

the vegetation type exerts a strong influence on the thickness of surface horizons.

Thickness of subsoil horizons varies a great deal in each zone but follows the same general pattern of increasing thickness with increasing altitude. On the west end of the mesa the clay subsoils are exceedingly thick but the rocky nature of the soil made it impractical to determine how thick.

Subhorizons such as the  $A_3$  in the park soils on the mesa vary a great deal but may be as much as 10 inches thick in places.

It is possible that the cobbly alluvial deposits below the rim may have favored development and thickness of horizons in comparison to consolidated rock on the mesa. Since these below-rim deposits, however, are similar in degree of

consolidation and there is a wide variation in the thickness of their soil horizons, it is apparent that horizon thickness can be attributed to other causes.

### *Colors*

In sharp contrast to the dark gray and black colors of adjacent soils developed from shales, soils developed from basalt contain much red and brown. This is true even of soils in the shadscale zone. Colors of the profile horizons are given in table 1. Surface soil colors become darker with increasing altitude. In the field, subsoil colors appear brightest in the shadscale, pinon-juniper, and oak brush zones. In the soils of the grass parks on the mesa, the A<sub>3</sub> is pale yellowish brown. An irregular, distinctly gray layer 1 or 2 inches thick occurs between the claypan and the A<sub>3</sub> in park soils developed from bedrock. This gray lens is also found in the poorly drained meadow soils on the mesa but is absent in all other soils.

The A horizon colors of soils developed under spruce are lighter than those of adjacent grassland soils. This is more commonly true of those soils above 10,400 feet. Surface colors of the wet meadow soils range from dark gray to black (fig. 3C).

### *Textures*

A high silt content is characteristic of surface soils developed from basalt. All surface soils in all zones are loams. Field observations indicate that most subsoils are very high in clay, but the data in table 2 indicate that the percentage of clay is not overly high in four profiles selected as typical. Field conditions suggest less favorable subsoil relations than are normally associated with clay loams. For example, those soils on the west end of the mesa have definitely restricted internal drainage due to a dense claypan. To a lesser degree this is true of soils developed from old till. The clay subsoils are often several feet thick, the only changes with depth being an increase in rock content and a decrease of the brown color. In the lower subsoil the basalt rocks are severely weathered, some being soft enough to cut with a knife or break with the hands. Subsoils in the shadscale are clay loams or clays, but they are open and friable in comparison to those on the mesa. Clays have not accumulated in the B horizon of soils from new till, and clays in the subsoils in the glaciated area are found only occasionally.

All soils contain a high percentage of rock on the surface, in the solum, and in the parent material. Below the rim the drift rocks range in size from those weighing several tons to fine gravel. On the mesa, bedrock protrudes in many places. In the glaciated area these protruding rocks occupy an estimated 10 to 30 per cent of the total area. Profile uniformity is interrupted in many places by these rock protrusions.

### *Structure*

A granular structure is common to the surface soils throughout all zones. The granules are most distinct in the shadscale and in the park soils on the

mesa. In the shadscale zone, beneath the platy, vesicular surface crusts, the units are small, distinct, and firm; in the parks they are medium in size, soft, and less distinct. In nearly all places the granules increase in size but become less distinct in the lower part of the surface soil.

Clay subsoils in all zones have a distinct large to very large blocky structure in the upper few inches. This is most distinct in the pinon-juniper zone. In all zones the units become less distinct with depth and change to a massive condition. This is particularly true in the thick subsoils on the mesa which

TABLE 2  
*Mechanical composition of selected profiles developed from basalt\**

PROFILE	HORIZONS AND DEPTH	GRAVEL† AND ROCK > 2 MM.	SAND 2.0- 0.05 MM.	SILT 0.05- 0.002 MM.	CLAY < 0.002 MM.
	<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Basalt drift (pinon-juniper)	A 0-3	10.5	41	46	13
	B <sub>1</sub> 3-9	5.7	32	44	24
	B <sub>2</sub> 9-15	0.6	32	48	20
	B <sub>3</sub> 15-30	3.4	28	45	27
Basalt drift (oak brush)	A 0-12	18.8	40	51	9
	B 12-36	49.7	36	39	25
Basalt bedrock (grass parks)	A <sub>1</sub> 0-18	0.9	35	61	4
	A <sub>3</sub> 18-28	0.8	38	54	8
	B <sub>1</sub> 28-34	0.8	38	45	17
	B <sub>2</sub> 34+	40.1	35	35	30
New till (grass parks)	A 0-18	7.3	36	56	8
	B 18-34	43.9	38	54	8
	C 34+	43.5	54	40	6

\* Analysis by hydrometer.

† Gravel calculated as percentage of entire sample; sand, silt, and clay calculated on basis of material <2 mm.

never become dry. Subsoils in the shadscale and pinon-juniper zones are subject to alternate wetting and drying.

In the shadscale zone the subsoil structure is a mixture of granules and small blocks. This rests upon a layer of less distinct structure which is very high in lime and gypsum in the lower part. The gypsum appears to result from the influence of the underlying mancos shales. Not infrequently the lime accumulates in firm to hard irregular plates which may lie horizontal to the surface.

#### *Organic matter<sup>4</sup>*

The organic matter content (table 1) reflects the changes in type and density of vegetation with increasing altitude. The percentage of organic matter in

<sup>4</sup> Determinations of organic matter, pH, and mechanical analysis were made by Harold L. Parkinson, who is in charge of the soils laboratory maintained by Soil Conservation



the surface soils increases from 1.3 in the shadscale zone to 6.1 in the mesa parks. The lower organic content of 4.4 and 4.5 for the park soils developed from old and new tills is without a ready explanation. Although soils developed under spruce appear to be low in organic matter, the analysis shows considerable amounts. The wet meadow soils on the mesa have the highest content of organic matter. The 7.7 per cent value increases in places, since these soils often grade into peat.

### *Reaction*

There is little variation in pH between the horizons of the same soil regardless of its zone. Distinct variations do occur between soils in different zones, as shown in table 1. Reaction of the surface soil varies from pH 8.2 in the shadscale zone to about pH 6.5 in the parks on the mesa.

All horizons of the solum in the shadscale zone effervesce, and lime is accumulated in thick crusts over rocks. Gypsum sometimes occurs in the C horizon. In the pinon-juniper zone, lime occurs as blotches and nodules in the lower part of the B horizon. It accumulates as crusts on the underside of cobbles. Free lime is absent from the solum and the underside of cobbles in the oak brush, and is rarely found above the oak. Despite the increased moisture and high altitude there is no distinct podzolization under spruce on the mesa below 10,400 feet. Above this approximate elevation the soils become increasingly acid with occasional values of pH 4.5 (colometrically determined). In this case the most acid part of the profile is not specific in its location or associated with a particular color change. Under spruce the duff is always more basic than the surface soil. Since it is known that other soils under spruce at lower elevations but from different parent materials develop strongly acid profiles, it is concluded that the basalt parent material exerts a strong influence on the reaction of soils which develop from it.

### DISCUSSION

The effects of climatic-vegetal differences from the desert upward are reflected by increasing thicknesses of horizons and increasing organic matter contents of the surface soils. This relationship is common to soils developed from basalt as well as soils from many different parent materials. Although the parent materials beneath the rim are not so consolidated as those on the mesa, it appears that this difference is minor in comparison to other factors influencing soil development. Slopes are much steeper beneath the rim, and natural erosion has probably been more rapid there than on the mesa. It has been slow enough, however, to permit distinct subsoils to develop. Likewise there is considerable uniformity in the thickness of surface soils within each zone, irrespective of considerable variation in local relief. The protection resulting from the dense

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Service in cooperation with Colorado A & M College. Organic matter determined by potassium dichromate oxidation and subsequent reduction with ferrous ammonium sulfate and reoxidation with potassium permanganate.



cover of oak brush and aspen under natural conditions appears to have held natural erosion to a minimum and permitted a full expression of the soil-forming factors.

The acidity of surface soils ranges from pH 8.2 in the shadscale zone to pH 4.5 above 10,400 feet. Subsurface horizons show a similar relationship. In view of the annual precipitation and type of vegetation on the mesa, the pH values would be expected to be lower. Since the soils are not overly acid and there is little displacement of bases within the profiles, as indicated by pH values, it is apparent that the high content of weathering basaltic rock has been an important factor in soil development. This rock is a constant source of base replenishment, which is not overcome by leaching except above 10,400 feet.

The red and brown soil colors strongly reflect the iron in the parent rock throughout all zones.

The silt content of all horizons is high. Even horizons that contain larger percentages of clay are high in silt. If a concentration of clay in the subsoil is accepted as one measure of soil maturity, then all the well-drained soils studied appear to be mature except those developed from new till and those in the glaciated area. These latter two cases strongly suggest that the time factor has not been sufficiently great to permit mature development. Hydrolysis of the parent rock minerals in place appears to be a logical explanation for a large part of the clay development. This is supported by the extreme thickness and density of the clay subsoil, the character of rock weathering, and the general lack of low pH values throughout the profile. On the other hand, the abruptness and density of the top of the claypan in most soils, especially those on the mesa top, suggest that eluviation may also be an active process. If so, conditions for the development of claypans would be most favorable on the mesa where the soils are very wet for a considerable period in the spring. Because of high lime content in the pinon-juniper soils and very high lime and gypsum in the soils of the shadscale zone, eluviation of clays is probably not an important process in subsoil development in these zones.

Many mountain soils contain large quantities of rock which are ordinarily not taken into account in the conventional method of reporting mechanical analyses. The percentage of rock in the total sample for the soils analyzed is shown in table 2. Even these values are low because it is customary to discard the larger rocks in collecting samples. From these and other studies it is apparent that rock occupies a considerable volume of the profile and probably has a marked influence on infiltration and internal moisture relationships.

Ecologically it appears that spruce in contrast to grass has exerted little influence on soil development on the mesa below 10,400 feet. There is little difference in pH values or organic matter content between the two soils, but colors of the surface soils do appear to be lighter under spruce. Spruce is as vigorous where the subsoils are heavy clays as where they are loose and open as in the new till belt. It appears logical to attribute the increased soil acidity above the general 10,400 feet elevation to an increase in precipitation and not to the effect of vegetation.

Soil development is related to recent geological events of the area. The west end of the mesa has never been glaciated, and therefore soil development must have been continuous since the lava flow in late Tertiary or very early Pleistocene time. Claypans are thickest and best developed here. To the east, clay subsoils are moderate to well developed in the old till but internal drainage appears to be less restricted than in the unglaciated area. The new till area has no clay accumulation in the solum (table 2). The area east of the new till was covered by a third ice sheet of a local nature which carved many valleys and seemingly carried its load over the north and south rims. Thus the new till and the glaciated areas have apparently not been in place or free of glacial action long enough to allow soils to develop to maturity. Topographic positions of the areas beneath the rim suggest stable conditions from early Pleistocene, and these areas have soils with mature profiles. If a relationship is assumed between the time factor involved in developing claypans in the soil on Grand Mesa and those in the Middle West (the Putman and Herrick soils for example), then a time relationship probably exists between the Kansan or Illinoian glaciations and the glacier which laid down the old till on the mesa. Certainly soil development and characteristics strongly supplement other evidence on the ground in establishing three periods of glaciation for the mesa.

It was found that site conditions of the Grand Mesa have been sufficiently stable over time to enable most of the soils to develop to maturity. This is checked against immature soils developed under identical conditions but from parent materials recently disturbed by glacial action. Except for differences in the degree of consolidation above and below the rim, the basaltic parent rocks are identical throughout. Marked differences in profile characteristics occur from the desert shadscale zone at 5,000 feet to the high spruce zone at approximately 10,800 feet. It is concluded that these differences are a reflection of the vegetal-climatic factors acting on a specific type of parent rock.

#### SUMMARY

A study was made of soils developed from basalt adjacent to and on the Grand Mesa in western Colorado, where elevations range from 5,000 to about 10,800 feet. These studies showed that the thickness of the A horizons increases with increasing altitude from about 6 inches to more than 16 inches; the reaction decreases from about pH 8 in the desert to pH 4.5 in extreme cases under spruce above 10,400 feet; the organic matter increases from 1.3 per cent in the desert to about 6 per cent on the mesa; subsoil development tends toward claypans, reaching a maximum development on the mesa; and the effects of the time factor are strongly evident in that some soils developed from recent glacial till have not developed clay subsoils.



# EXCHANGEABILITY OF ADSORBED CATIONS AS INFLUENCED BY THE DEGREE OF SATURATION AND THE NATURE OF THE COMPLEMENTARY IONS WITH SPECIAL REFERENCE TO TRACE CONCENTRATIONS<sup>1</sup>

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The exchangeability of ions at extremely low degrees of saturation is vitally important in plant nutrition. This applies particularly to the relationships between plants and the essential minor elements in soils. Studies on traces of ions in exchange systems have been neglected as a result of the failure of the classical microanalytical methods to provide sufficient precision for the measurement of traces of adsorbed and exchanged ions. These difficulties were overcome in this study by using certain radioactive cations as tracers in exchange reactions involving minute concentrations.

In order to study the exchange of cations at very low degrees of saturation it was necessary to select an "ideal exchanger." Amberlite IR-1 was selected for this purpose because it shows no crystal lattice type of cation fixation. Clay minerals and other natural cation exchangers have a tendency to fix ions, in difficultly or nonexchangeable form, in the crystal lattice. This fixation can be very strong, especially when the adsorbed ion happens to encounter voids in the crystal lattice which exhibit the proper size, charge, and coordination for the incoming ion.

There has developed a rather commonly accepted opinion that an exchangeable ion always becomes more and more difficult to replace as its concentration on the surface of the exchanger becomes less. This has been considered to be the case without regard to the nature of the other adsorbed ions, the so-called *complementary* ions. At very low concentrations on the exchange surface, the ion must, according to this opinion, become extremely difficult to replace. Results from experiments carried out by Weisz (7), Yarussov (9), Schachtschabel (6), and Damsgaard-Soerensen (2) have been interpreted by these authors as a proof of this concept.

<sup>1</sup> Contribution from the department of agronomy, University of Illinois Agricultural Experiment Station. Published with the approval of the director of the Illinois Agricultural Experiment Station.

<sup>2</sup> Swedish American Foundation fellow and A. J. Roman fellow from the department of pedology of The Royal Agricultural College of Sweden, Uppsala, Sweden.

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The radioactive potassium and strontium were supplied by the Isotopes Branch of the United States Atomic Energy Commission, Oak Ridge, Tennessee.

Shipments of radioactive potassium were sufficiently large to permit sharing with C. L. Prosser of the department of zoology. R. B. Duffield, of the department of physics, furnished the radioactive strontium from an excess supply obtained for instructional purposes. The writers are indebted to C. L. Prosser and R. B. Duffield for their cooperation and to the departments of physics and chemistry for certain equipment used in this investigation.



Among the first to take interest in the problem of the influence of the complementary ions on the uptake of ions by plants were Horner (3), Yarussov (10), and Mehlich and Colwell (5). This problem has also been considered by Jenny and Ayers (4) in experiments and theoretical discussions. Later Bray (1) studied the release of ions from soils at low percentage replacement and discussed ionic competition in base-exchange reactions.

#### THEORETICAL

The factors determining the release of adsorbed ions were studied by Wiklander (8) in experiments with several different ion combinations on artificial and natural ion exchangers. By application of the activity concept and the law of mass action, it was found that the exchangeability or the percentage replacement of any adsorbed ion ( $M$ ), on addition of a small quantity of an electrolyte, is determined by:

1. The ease of release of the ion ( $M$ ) as expressed by the activity coefficient of the ion in the adsorbed condition. The activity coefficient is determined by the radius, the valence, and the hydration of the ion as well as by the ionic strength. The lower the activity coefficient of a certain ion in relation to that of the complementary ions, the more difficult will be the replacement of the ion.
2. The degree of  $M$  saturation ( $D$ ), expressed in percentage of the total amount of exchangeable ions. The greater the difference between the activity coefficient of a certain ion and that of the complementary ions, the more the exchangeability of the ion will be influenced by a varying degree of saturation.
3. The valence of the ion  $M$  in relation to the valence of the complementary ions.
4. The nature of the complementary ions as expressed by the activity coefficient of these ions, in the adsorbed condition, and their valence. The exchangeability of an adsorbed ion increases if an ion with a low activity coefficient is substituted for a complementary ion with a high activity coefficient. On the other hand, the exchangeability decreases if an ion with a high activity coefficient is substituted for a complementary ion with a low activity coefficient.

From this it follows that the exchangeability of an ion on an ideal exchanger should increase in the order:



when these ions function separately as complementary ions (fig. 1). This is true because the activity coefficients of these ions decrease in the direction from Li to La.

5. The exchange capacity, so far as it determines the concentration of the micellar solution or the exchanger phase, in case of dissimilar valence of the adsorbed ions.
6. The total amount of replaced ions.

In case the colloid is saturated with two ions,  $M_1$  and  $M_2$ , of the same valence, a more detailed analysis of the relationship mentioned will show that when the degree of  $M_1$  saturation *decreases*, the exchangeability of this ion may *increase*, be *unchanged*, or *decrease*, depending on the relative magnitude of the activity coefficients of the two ions. When the  $M_1$  saturation decreases, the exchangeability of  $M_1$  will increase if the activity coefficient of  $M_1$  is greater than that of  $M_2$ ; it will be unchanged if they have the same value; and it will decrease if the activity coefficient of  $M_1$  is less than that of  $M_2$ . The replacement of sodium and potassium from a cation exchanger, saturated with these two ions, may be taken as an example of the first and third cases mentioned.



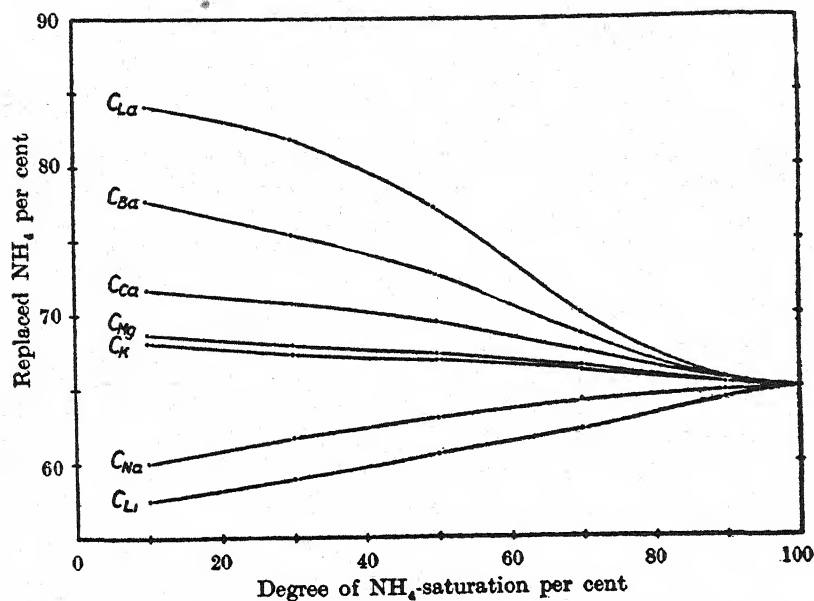


FIG. 1. INFLUENCE OF THE COMPLEMENTARY ION AND THE DEGREE OF SATURATION ON THE RELEASE OF  $\text{NH}_4$ , ON ADDITION OF A CONSTANT AMOUNT OF  $\text{HCl}$ , FROM RESIN SATURATED WITH  $\text{NH}_4$ , PAIRED WITH EACH OF THE FOLLOWING IONS: Li, Na, K, Mg, Ca, Ba, AND La  
 $C_{Li}$ ,  $C_{Na}$ , etc. mean the complementary ions. From Wiklander (8)

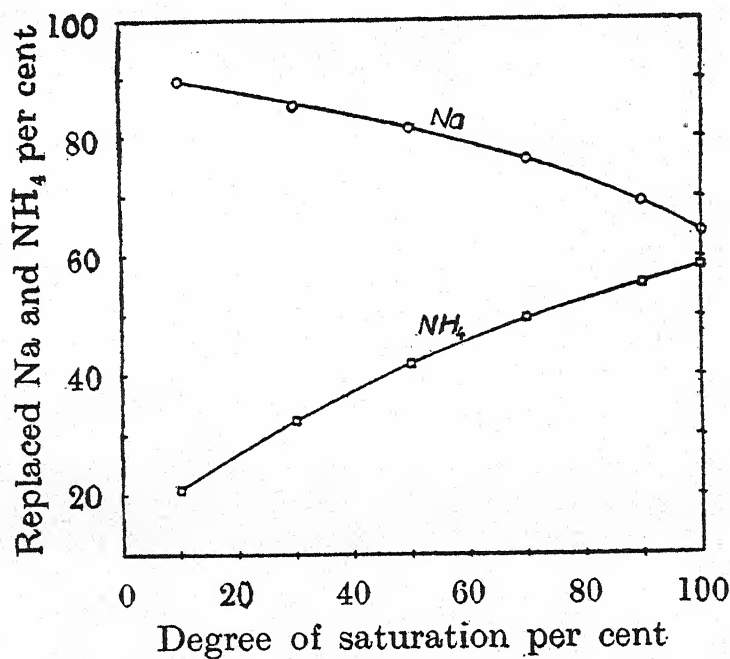


FIG. 2. REPLACEMENT OF  $\text{NH}_4$  AND  $\text{Na}$ , WITH  $\text{HCl}$ , FROM PERMUTITE SATURATED WITH THESE IONS IN VARIOUS PROPORTIONS

From Wiklander (8)

The ratio of the activity coefficient of sodium to that of potassium was found by Wiklander (8) to be 1.96 when a resin type of exchanger was used. This is in accordance with the stronger replacing power of potassium. If a certain amount of electrolyte is added to a Na- and K-saturated exchanger, the percentage of Na replaced becomes higher as the degree of Na saturation becomes lower. In case the exchanger is saturated with Na only ( $D_{Na} = 100$ ), a minimum percentage of Na will be released, but when the Na content decreases, the replacement increases and approaches a maximum value at low degrees of Na saturation ( $D_{Na} \rightarrow 0$ ). For potassium, on the other hand, the conditions are reversed. The exchangeability has a maximum value when the exchanger is saturated with potassium ( $D_K = 100$ ,  $D_{Na} = 0$ ); it decreases with falling degree of K saturation; and it approaches a certain minimum when  $D_K$  approaches 0.

The same conclusions can be drawn for any other ion pairs or ion combinations if the activity coefficients are unequal.

A few of the experimental results from Wiklander (8) are given here (figs. 1 and 2) because of their close connection with the present paper.

It is apparent from the figures that the results and the theories are in good agreement. Because of analytical difficulties, however, it was not possible in these early experiments to go to degrees of saturation lower than 7 per cent. It is the purpose of this investigation to study the replacement of cations at very low degrees of saturation, thus covering the range below  $D = 7$  per cent, by using radioactive isotopes as tracers.

#### EXPERIMENTAL

##### *Methods*

The experiments were carried out with the cation exchange resin, Amberlite IR-1, a phenol-formaldehyde polymer containing free methylene-sulfonic acid, carboxyl, and phenolic groups. This product shows no crystal lattice type of ion fixation, the adsorption equilibrium is reversible, and the rate of exchange reaction is high. These characteristics make it suitable for this investigation.

The Amberlite was first treated with HCl and then washed carefully with distilled water. Most of the hydrogen ions on the air-dried H-Amberlite were neutralized with 150 m.e./100 gm. of the four following pairs of ion combinations respectively: K-Na, K-Ba, Sr-Na, and Sr-Ba. The proportions of each ion in each pair were varied over an appropriate range (tables 1 and 2). The first two series contained sufficient radioactive potassium for convenient measurements, and the last two contained radioactive strontium. The saturation was performed in the reaction flasks, the Amberlite being moistened one day before, by adding the calculated amounts of the ions in the form of hydroxides or carbonates. Because of the short half-life of radioactive potassium, 12.4 hours, special precautions were taken by reserving part of each radioactive solution used in these experiments for subsequent use as controls. After 3 hours of repeated shaking for the K series, and 24 hours of shaking for the strontium series, part of the adsorbed ions were replaced by adding HCl to the reaction flasks. After another 3 hours' shaking in the same manner, the activity of

radioactive potassium in the supernatant liquid was determined by use of a Geiger-Müller counter with the sample in an annular-ring type of vessel surrounding the tube. The radioactivity of the control was always measured in the same annular ring immediately following the corresponding measurement

TABLE 1

*Replacement of radioactive potassium from Amberlite of various degrees of K saturation by adding 6 m.e. of HCl to a system containing 2 gm. of air-dried H-Amberlite + 3 m.e. of base, total volume 100 ml.*

SATURATING IONS	DEGREE OF SATURATION					
K.....per cent	0.1	1	5	10	50	99.9
Na.....per cent	99.9	99	95	90	50	0.1
Added K.....m.e.	0.003	0.03	0.15	0.3	1.5	2.997
Added Na.....m.e.	2.997	2.97	2.85	2.7	1.5	0.003
K replaced.....per cent	39.9	40.4	40.8	42.1	44.8	50.3
K.....per cent	0.1	1	5	10	50	99.9
Ba.....per cent	99.9	99	95	90	50	0.1
Added K.....m.e.	0.003	0.03	0.15	0.3	1.5	2.997
Added Ba.....m.e.	2.997	2.97	2.85	2.7	1.5	0.003
K replaced.....per cent	68.1	68.5	67.4	67.4	59.5	49.9

TABLE 2

*Replacement of radioactive strontium from Amberlite of various degrees of Sr saturation by adding 7.5 m.e. of HCl, the same proportions as in table 1, except for HCl*

SATURATING IONS	DEGREE OF SATURATION						
Sr.....per cent	$10^{-9}$	0.1	1	5	10	50	99.9
Na.....per cent	100	99.9	99	95	90	50	0.1
Added Sr.....m.e.	$3 \times 10^{-11}$	0.003	0.03	0.15	0.3	1.5	2.99
Added Na.....m.e.	3.00	2.997	2.97	2.85	2.7	1.5	0.003
Sr replaced.....per cent	4.82	4.85	4.96	5.24	5.81	12.1	31.5
Sr.....per cent	$10^{-9}$	0.1	1	5	10	50	99.9
Ba.....per cent	100	99.9	99	95	90	50	0.1
Added Sr.....m.e.	$3 \times 10^{-11}$	0.003	0.03	0.15	0.3	1.5	2.997
Added Ba.....m.e.	3.00	2.997	2.97	2.85	2.7	1.5	0.003
Sr replaced.....per cent	39.5	39.0	38.4	37.7	—	34.6	31.6

on the unknown. Percentages of exchange were calculated from comparisons with the control solutions which had not been contacted with the resin.

Radioactive strontium has a more complicated decay than potassium, which made it necessary to introduce certain divergences from the procedure given for potassium. The radioactive strontium was chiefly isotope 90 with a 25-year half-life. It decays to radioactive yttrium, with a 62-hour half-life, which then decays to give stable zirconium. Part of the yttrium is adsorbed by the resin and causes a change of the radioactivity of the supernatant liquid, which would

not occur in the control. This error was avoided by transferring the supernatant liquid to flasks where it was kept for 14 days, thus allowing the decay chain to reach the same equilibrium between Sr 90 and Y 90 as would be found in the control.

### Discussion of results

The potassium carbonate obtained from Oak Ridge contained a very low concentration of radioactive potassium. Consequently, the lowest measurable value that could be used for potassium was 0.1 per cent of saturation. On the other hand, it was possible to use an extremely low concentration of the strontium

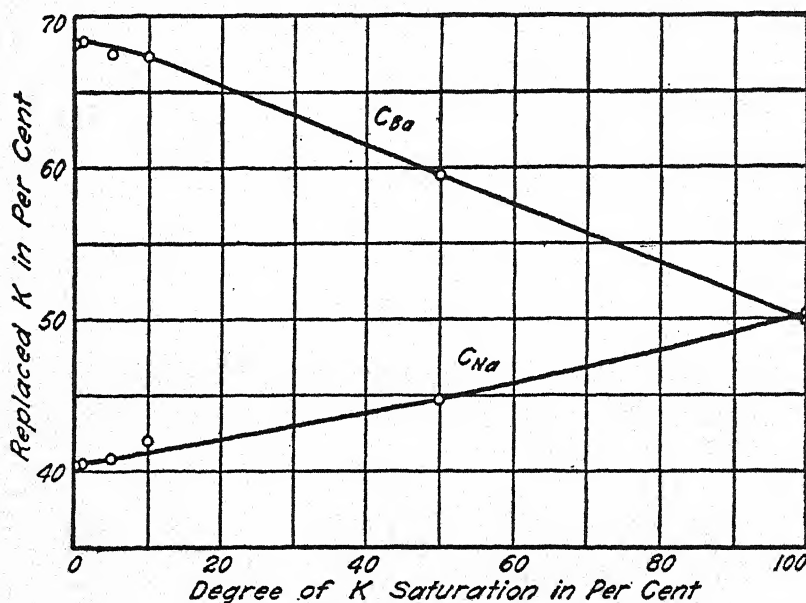


FIG. 3. CHANGE OF PERCENTAGE REPLACEMENT OF K, ON ADDITION OF A CONSTANT AMOUNT OF HCl, FROM AMBERLITE SATURATED IN VARIOUS PROPORTIONS WITH K—Na AND K—Ba, RESPECTIVELY

ion because the sample of strontium was not contaminated with inactive strontium (tables 1 and 2, figs. 3 and 4).

It appears from table 1 and figure 3 that with falling K saturation, the exchangeability of potassium decreases when combined with sodium, but increases strongly when combined with barium. This is in agreement with the results found earlier as well as with the theory. This is accounted for by a higher activity coefficient of sodium than of potassium and a higher activity coefficient of potassium than that of barium. In the latter case, it is likely that the difference in valence also plays an important role.

Strontium shows the same relationships as potassium. Because the activity coefficient of strontium is greater than that of barium and the activity coefficient of sodium is greater than that of strontium, the percentage release of strontium, with diminishing saturation, increases when combined with barium but decreases



strongly when coupled with sodium. The valence effect has probably contributed to this marked decrease in the latter case.

The replacement curves approach certain maximum and minimum limit values when the concentration of an ion on the exchange surface becomes very low ( $D \rightarrow 0$ ). This is especially apparent for strontium with its extremely small concentration at the lowest value.

In this paper activity coefficients have been used as an expression for the properties of ions so far as ease of replacement is concerned. Since there seems

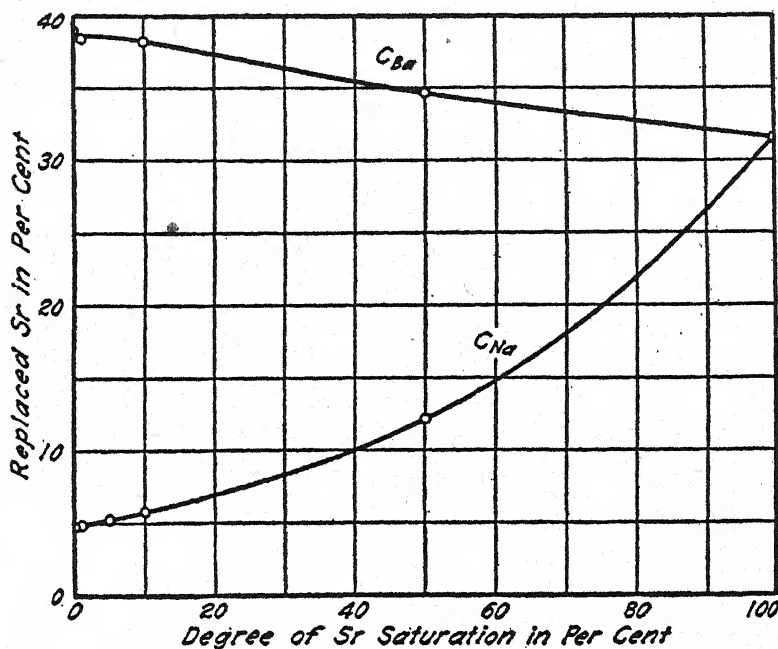


FIG. 4. REPLACEMENT OF Sr, WITH HCl, FROM AMBERLITE SATURATED WITH Sr-Na AND Sr-Ba, RESPECTIVELY, IN VARIOUS PROPORTIONS

to be a close relationship between the activity coefficients and the replacing power of ions (8), it is possible to use the latter for qualitative discussions concerning the release of adsorbed ions. If the mutual replacing power of two ions differs, the exchangeability of the ion with the lower adsorptive intensity will increase, but the exchangeability of the ion with higher adsorptive intensity will decrease with a falling proportion of either ion. In case the nature of the complementary ions varies, the exchangeability of a given ion ( $M$ ) will be affected. Suppose we consider the ions  $M_1, M_2, M_3 \dots M_n$ , the replacing power of which increases in the following order:  $M_1 < M_2 < M_3 < \dots M_n$ . The ion ( $M$ ), when combined with one or more of these ions, will become more and more easily replaced as the proportion of the complementary ions moves from  $M_1$  to  $M_n$ .

The present experiments were carried out with an exchanger which showed no fixation of the ions used. To make similar experiments with soils, it is



necessary to consider a possible crystal lattice type of fixation of added cations. This is particularly important at very low degrees of saturation. The fixation of K and  $\text{NH}_4$  by soil clays has been found (8) to introduce considerable error even at degrees of saturation approximating 10 per cent. As the degree of saturation decreases, the error resulting from fixation will become greater and greater. The relationships found to be valid in Amberlite can be applied only to that fraction of the exchangeable ions in soils which is easily exchangeable. It is very important, therefore, to consider fixation in studying the distribution of ions between soils and solutions at very low relative concentrations of the ions in question.

#### SUMMARY

The factors determining the exchangeability of adsorbed ions are discussed.

The exchangeability of ions adsorbed on Amberlite at very low degrees of saturation was studied. This was made possible by use of radioactive K and Sr, Na and Ba being used as complementary ions in both cases.

It was found that with decreasing K content, the exchangeability of K decreases when Na is the complementary ion, but increases when Ba is the complementary ion.

In the same way the exchangeability of Sr decreases with falling Sr content when combined with Na, but increases when combined with Ba. For both K and Sr, the percentage replacement approaches a limit value at very low degrees of saturation.

The experiments show that the exchangeability of an ion approaches a certain limit value when the concentration of the ion grows infinitesimally low. The magnitude of this limit is determined by the nature of (a) the ion itself, (b) the complementary ions, and (c) the ion exchanger.

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## DETERMINATION OF MAGNESIUM BY THIAZOL YELLOW METHOD<sup>1</sup>

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Methods for the quantitative determination of Mg, whether gravimetric or colorimetric, have always been tedious and time-consuming. There has long been need for more rapid yet equally reliable methods for the estimation of this element. The purpose of this contribution is to present such a method. In this procedure, Mg is determined spectrophotometrically as a colored Mg-lake with thiazol yellow, after precipitation and removal of interfering ions as insoluble tungstates.

### PRELIMINARY INVESTIGATIONS

A number of gravimetric and colorimetric methods for Mg were studied. None were found to be entirely satisfactory for routine use in rapid analyses of plant tissues and soil extracts. The former are too time-consuming and the latter possess two outstanding disadvantages: the dyestuffs in common use are poorly selective to the Mg ion, except over a narrow range of its concentration; and a number of interfering substances, such as Ca, Al, Fe, Mn,  $\text{NH}_4$ , and  $\text{PO}_4$ , affect the color that is formed and, accordingly, have to be removed before reliable Mg values can be obtained.

A search was made for new organic compounds that could be used for the colorimetric determination of Mg. More than 140 dyestuffs were investigated with respect to their selectivity to the Mg ion. Thiazol yellow (sodium 2-2-disulfonate of methylbenzothiazole),<sup>2</sup> was the most selective one found (3). In an alkaline medium the Mg ion forms a lake with the dyestuff that is adsorbed on the precipitate of  $\text{Mg}(\text{OH})_2$ . The color range produced is from pale orange through scarlet, depending on the Mg concentration. When measured spectrophotometrically, the extinction values obtained are linear over a range of 1 to 6 p.p.m. Mg. Beyond 6, the curve tends to deviate slightly from the linear relation to a maximum of 11 p.p.m. Mg. This is due to the heterochromaticity of light in the higher Mg concentrations. Starch solution is effective in adding stability to the colored lake. Hydroxylamine hydrochloride additions also aid in stabilizing the colored lake by reducing the fading of the color and inhibiting oxidation in the alkaline solution (2). Like all reactions of this type, conditions for the formation of colored lakes with respect to their stabilization and the development of color with time must be strictly followed for reproducible results. The stabilizing agents, the pH range best suited for the development of color,

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils, New Brunswick, N. J. Acknowledgment is due David D. Long, Chief of Feed and Fertilizer Research, International Minerals and Chemical Co., for his encouragement of this work and to the Company for partly financing the project.

<sup>2</sup> Produced by General Aniline Works, Rensselaer, New York.

and the influence of various other factors have been studied and delineated in this procedure.

The dyestuff, thiazol yellow, although more selective to Mg than any other dyestuff studied, is subject to the same interferences as are encountered with other colored Mg-lake reactions (2, 5, 6). The interfering effects of the ions are variable, but their specific interferences seem to be a function of the Mg concentration. Ca and Al, when present, usually result in abnormally high Mg values. Their effect is most pronounced at high Mg concentrations. Iron and Mn usually result in low Mg values. They are removed, however, as insoluble tungstates, and the interference of trace quantities that may still exist in solution are compensated for by the addition of hydroxylamine hydrochloride. The  $\text{PO}_4$  ion causes maximum interference when present in excess of 20 p.p.m. This is overcome by introducing  $\text{PO}_4$ , at a concentration of 20 p.p.m., in the sodium tungstate-buffer solution.

Britton and German (1) studied the precipitation of complex tungstates of the alkali and heavy metal cations. All of these cations except Mg are precipitated as tungstates at a pH value that is lower than the pH at which the corresponding hydroxides of the cations are formed. Use has been made of the formation of insoluble Ca tungstate for the estimation of Ca (4).

Removal of interfering ions by tungstate additions was carefully studied to determine whether the procedure could be adapted for routine use. It was found that the most favorable reaction range for the precipitation was pH 5.0 to 6.5. In the proposed procedure, this reaction range is established in the unknown solutions by addition of a mixture of sodium tungstate and sodium phosphate solutions.

The advantage of the proposed method for determining Mg is that, in a single operation, the interfering ions are removed as insoluble tungstates and the Mg is directly determined in the supernatant liquid after centrifugation. The method is rapid and reliable and well suited for routine estimation of Mg in plant tissues and in soil solutions.

#### METHOD OF DETERMINATION

##### *Plant material*

Place a definite weight of oven-dried plant tissue in a 200-ml. tall Griffin Pyrex beaker. Add concentrated nitric acid (10 ml.  $\text{HNO}_3$  is usually sufficient for a 2-grm. sample), cover with a watch glass, and heat gently on a hot plate until no visible signs of solid material remain. At this point the solution is generally straw-colored. Remove beaker from the hot plate, add 70 per cent perchloric acid in a 2:1 nitric-perchloric acid ratio, replace the watch glass, and gently boil until clear and fuming with copious vapors of perchloric acid. Generally the volume at this point is about 1-3 ml. Avoid allowing the solution to go to dryness. Add 25 ml. of distilled water, bring to boil, and pass through a Whatman No. 40 filter paper into a 100-ml. volumetric flask. Wash silica with hot water to about 75 ml. Cool, dilute to 100 ml.

*Exchangeable Mg*

Displace exchangeable cations from the soil by the Schollenberger method (7). Evaporate the extract to dryness and drive off the  $\text{NH}_4$  salts by heating. Oxidize residual organic matter by use of a 2:1 ratio of nitric and perchloric acids, as in the plant-tissue method. Take up the clear solution with hot water, filter while hot, and dilute to 100 ml.

This digest may be also used, with proper dilution, for estimating Na, K, and Ca in a flame photometer (8).

## REAGENTS AND SOLUTIONS

*Standard Mg solution (stock):* Dissolve 1 gm. of oxide-free Mg ribbon in sufficient HCl to bring about its solution. Make to 1000 ml.

*Standard Mg solution:* Dilute 100 ml. stock solution to 1000 ml.

*Thiazol yellow:* Dissolve 100 mgm. thiazol yellow in a small amount of water and make to 100 ml. Store in amber bottle.

*Sodium tungstate-buffer solution:* Dissolve 25 gm. c.p. sodium tungstate in 300 ml. water. Add 100 ml. 0.1 M trisodium orthophosphate. Make to 500 ml. Filter, if necessary, to give a clear solution.

*Starch solution:* A 2 per cent solution of soluble starch (boiled) is freshly prepared to give a colorless solution.

*Sodium hydroxide:* 3 N solution.

• *Hydroxylamine hydrochloride:* 5 per cent aqueous solution.

## REMOVAL OF INTERFERING CATIONS

Transfer a measured aliquot of the sample containing from 0.1 to 1 mgm. of Mg to a 15-ml. conical centrifuge tube. Add 5 ml. sodium tungstate-buffer solution and mix thoroughly by rotating the tube. Heat the tube in a water bath at 70°–80°C. for 15 minutes. Remove and add 3 N sodium hydroxide solution dropwise, while mixing the solution, until a crystalline precipitate forms. The pH at this point should not exceed 8.0. This can be determined by taking a separate aliquot of the digest, adding the sodium tungstate-buffer solution, one drop of bromthymol blue, and 3 N NaOH until the indicator changes at the proper pH. Place the tube in a water bath and digest for 15 minutes. Remove tube and centrifuge while hot, to throw down any suspended precipitate. Decant the supernatant liquid into a 50-ml. volumetric flask. Any flocculent precipitate formed should be washed repeatedly to free any coprecipitated Mg. Wash the precipitate with cold distilled water, centrifuge again, and decant the washings into the supernatant liquid collected previously.

Make combined solution up to a volume of about 30 ml. with water, and then add, in sequence with thorough mixing after the addition of each solution, 1 ml. starch solution, 1 ml. hydroxylamine hydrochloride solution, and 0.5 ml. thiazol yellow solution. Finally, add 2 ml. 3 N sodium hydroxide solution and make to volume. Each sample should be prepared in such a manner that it can be read in the spectrophotometer after exactly 20 minutes. Prepare a set of the standard solutions in the manner just described and read simultaneously with unknown.



Determine the light transmission by means of a colorimeter or spectrophotometer at a wavelength of 500  $m\mu$ .

#### STANDARD CURVE FOR Mg

A light-absorption curve for the developed color (fig. 1) shows that maximum absorption occurs at a wavelength of 500  $m\mu$ . Over a considerable range of Mg concentration, this maximum has been found to hold.

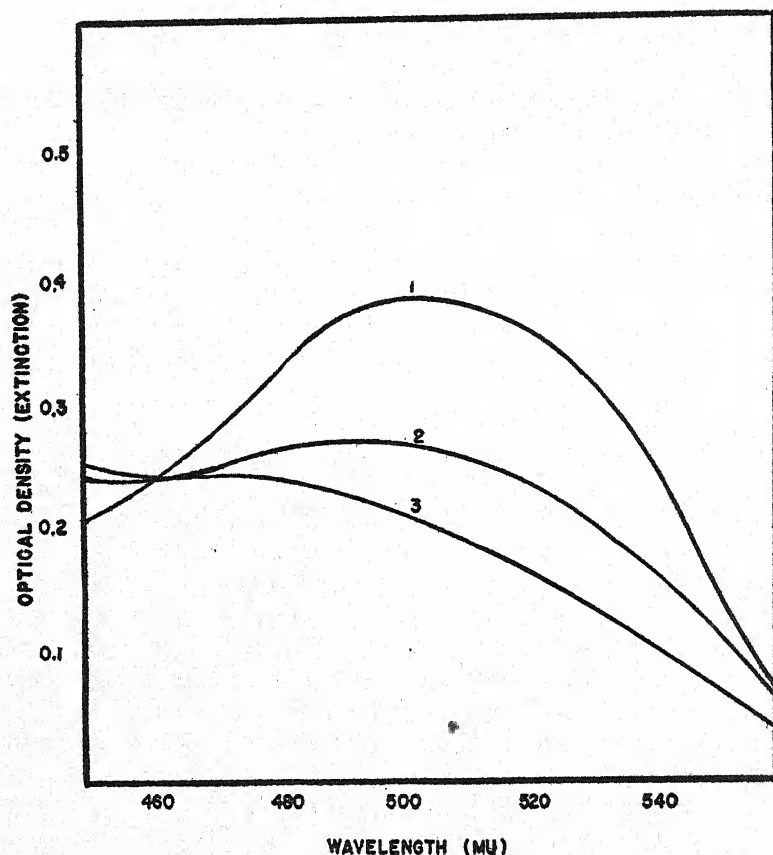


FIG. 1. SPECTRAL ABSORPTION CURVES OF THIAZOL YELLOW

1. Colored Mg-lake (9 p.p.m.) + thiazol yellow
2. Colored Mg-lake (3 p.p.m.) + thiazol yellow
3. Thiazol yellow

A standard extinction versus concentration curve for Mg, obtained with a model DU Beckman photoelectric spectrophotometer is shown in figure 2. The standard curve was made at a wavelength of 500  $m\mu$  and a slit width of 0.04 mm., using a 1-cm. cell. The curve does not pass through the 0 point of the intersection of the ordinate and abscissa, since the optical density versus concentration curve extinction values were determined against distilled water.



Several different batch samples of thiazol yellow were tested for their uniformity of color characteristics. It was found that sufficient differences exist between reagent lots that the standard curves must be checked each time a new sample of thiazol yellow is used. Some deterioration of the dye reagent also occurs in the presence of light, and occasional checking of the standard curve is essential from time to time. Adaptation of the thiazol yellow method

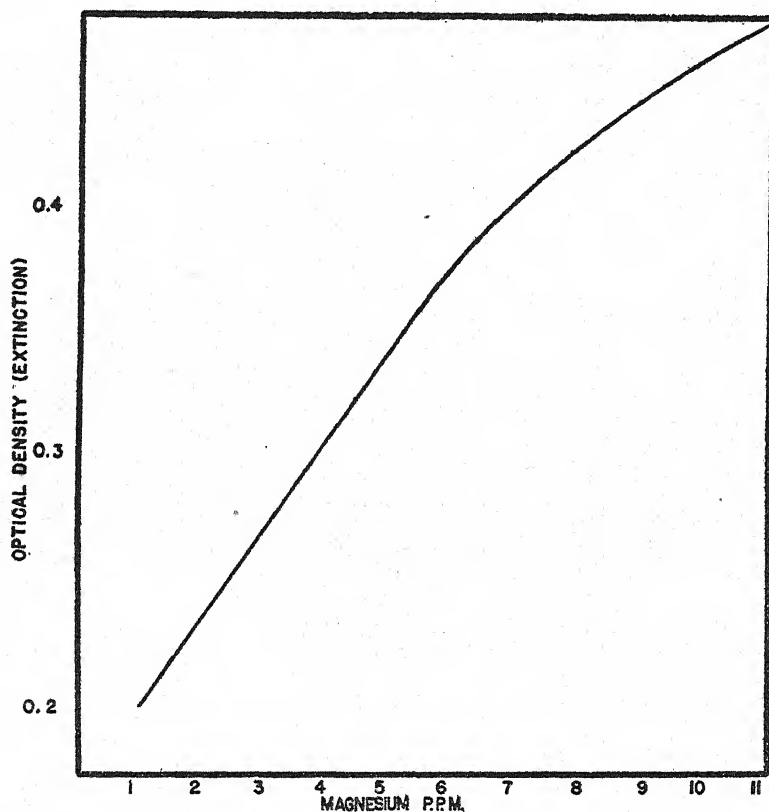


FIG. 2. STANDARD Mg CURVE WITH THIAZOL YELLOW  
Wavelength 500 m $\mu$ , slit width 0.04 mm.; 1-cm. cell

to colorimeters using filters of proper wavelength can be readily made, but with a loss of some sensitivity.

#### RESULTS AND DISCUSSION

The accuracy of the thiazol yellow method for Mg was compared with a standard gravimetric procedure.<sup>3</sup> The comparisons were made on: bean tissues of known Mg content; potato-leaf samples to which known quantities of Mg had been added; soil samples of known exchangeable-Mg content.

Data concerned with the analysis of bean tissue by the two methods are

<sup>3</sup> Precipitation as  $\text{MgNH}_4\text{PO}_4$  and ignition to  $\text{Mg}_2\text{P}_2\text{O}_7$ .

presented in table 1 and represent the averages for duplicate samples. Average recovery by the thiazol yellow method for six samples of bean tissue was 98.8

TABLE 1  
*Magnesium recoveries from bean-tissue by A.O.A.C.\* and thiazol yellow methods*

SAMPLE	A.O.A.C. METHOD	THIAZOL YELLOW METHOD	AVERAGE RECOVERY	DIFFERENCE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.19	0.20 0.18	100	0
2	0.24	0.23 0.24	98	-2
3	0.30	0.31 0.32	105	5
4	0.30	0.30 0.29	98	-2
5	0.37	0.35 0.34	98	-2
6	0.45	0.44 0.41	94	-6

\* Precipitation as  $MgNH_4PO_4$  and ignition to  $Mg_2P_2O_7$ .

TABLE 2  
*Recoveries by thiazol yellow method, of Mg added to potato-leaf tissues*

THEORETICALLY PRESENT	ACTUALLY FOUND	AMOUNT ADDED TO STANDARD	RECOVERY OF ADDED Mg	
<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>
0.175	0.173 0.179	0.0	-0.002 0.004	100
0.216	0.214 0.218	0.041	0.039 0.043	100
0.257	0.259 0.261	0.082	0.084 0.088	103
0.339	0.358 0.347	0.164	0.183 0.172	107
0.421	0.424 0.427	0.246	0.249 0.252	101

per cent. The recoveries ranged from 94 to 105 per cent. These results are typical of the accuracy that can be attained by this procedure.

Recoveries of known amounts of Mg added to potato-leaf samples are summarized in table 2. The average recovery from a series of five samples was 102.5 per cent.

Comparisons of the exchangeable Mg content of four soils are presented in table 3. The average recovery was 103 per cent.

The results of these three comparisons indicate that the thiazol yellow procedure is well suited for routine analysis of Mg in plant tissue and for exchangeable Mg in soils. The method is rapid and reliable.

The results shown represent only a small portion of the data that have been accumulated in this laboratory on the thiazol yellow method. The chief precaution to be observed in use of the method is that the system of the addition of the various reagents be strictly followed.

Earlier attempts to determine the Mg content of plant and soil extracts by the use of compensating solutions (3) were not satisfactory.

TABLE 3  
*Recoveries of Mg in soil extracts*

SOIL	A.O.A.C. METHOD	THIAZOL YELLOW METHOD	RECOVERY	DIFFERENCE
	<i>m.e.*</i>	<i>m.e.*</i>	<i>per cent</i>	<i>per cent</i>
Whippany.....	1.46	1.50	102	2
Gloucester.....	0.55	0.60	109	9
Lakewood.....	0.07	0.07	100	0
Bermudian.....	3.35	3.40	101	1

\* Per 100 gm. soil.

#### SUMMARY

A rapid colorimetric method for estimating the Mg content of plant tissue and soil extracts is presented.

The method involves removal of interfering ions by precipitation as insoluble tungstates and determination of Mg colorimetrically by use of thiazol yellow.

The colored Mg-lake formed shows maximum absorption at a wavelength of 500 m $\mu$ .

The relation between Mg concentrations in solution and optical densities is linear when measured spectrophotometrically, up to a concentration of 6 p.p.m.

Data obtained by the thiazol yellow method are accurate and reproducible.

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# PERSISTENCE OF ISOPROPYL N-PHENYL CARBAMATE IN SOILS<sup>1</sup>

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Isopropyl N-phenyl carbamate is a plant growth-regulator which inhibits the growth of many monocotyledonous and certain dicotyledonous species. For example, Ennis (3) found that 13 monocotyledonous species and 15 out of 39 dicotyledonous species showed some response to this compound when it was applied to the soil at planting time at a rate of 10 mgm. per 1.7 kgm. soil. Certain crops, including barley, timothy, buckwheat, and flax, failed to emerge from the soil, whereas 6 of the 15 affected broadleaf species largely recovered from the treatment. It has been suggested that isopropyl N-phenyl carbamate or similar compounds might be used as herbicides and for vegetational control.

The persistence of isopropyl N-phenyl carbamate when added to soil at the high rate of 50 pounds per acre has been studied by DeRose (1). In one field experiment the compound persisted more than 40 but less than 60 days, and in another experiment it persisted more than 68 but less than 90 days. Mitchell and Marth (4) similarly found that isopropyl N-phenyl carbamate added at a rate of 40.8 mgm. per pound of soil and incubated in the greenhouse persisted less than 2 months. Wolcott and Carlson (6) reported that the compound seems to be inactivated in the soil in 30 to 60 days, depending on the rate of application and the degree of aeration in the soil. Weaver (5) found that the toxicity of this carbamate at a concentration of 22 p.p.m. in a silt loam soil was greatly decreased by 12 days of storage.

The objective of these experiments was to investigate the effects of certain factors such as soil temperature, soil moisture, soil population, and the form and rate of the compound on the persistence of isopropyl N-phenyl carbamate.

## METHODS AND PROCEDURE

Purified isopropyl N-phenyl carbamate was used in all experiments except those on the form and rate of the compound, in which the technical grade<sup>3</sup> was used.

Persistence was determined by observations of emergence and plant response of oats, corn, and barley. The test crop was varied as noted in the individual experiments. Barley was the most sensitive crop, since a rate of 0.1 mgm. of isopropyl N-phenyl carbamate per pound of soil caused a slight stunting of this crop whereas the same rate had no effect on corn or oats. A 0.3 mgm. rate delayed the emergence of barley, though the barley subsequently recovered,

<sup>1</sup> Contribution from Camp Detrick, Frederick, Maryland.

<sup>2</sup> Agronomists.

<sup>3</sup> Furnished by Pittsburgh Plate Glass Company, Columbia Chemical Division, Pittsburgh, Pennsylvania.



and had no effect on corn or oats. A rate of 0.9 mgm. prevented the emergence of barley, delayed the emergence of oats, and had no noticeable effect on corn. A rate of 2.7 mgm. prevented the emergence of barley and oats and caused a moderate stunting of corn with subsequent death.

In experiments on the form of compound, the material was distributed evenly over the soil surface at rates of 10 or 50 pounds of active substance per acre. All the solid materials contained 50 per cent of the carbamate. The materials used were impregnated dust, nonimpregnated dust, extruded material, tributylphosphate solution, and aqueous solution. The impregnated dust was prepared by mixing a 95 per cent ethyl alcohol solution of the compound with Fuller's earth, evaporating the solvent, and then grinding the clay to a fine powder. The nonimpregnated dust was a simple mixture of the compound and Fuller's earth. The extruded material was prepared by mixing together 50 gm. isopropyl N-phenyl carbamate, 35 gm. Fuller's earth, and 5 gm. cornstarch to which was added 50 ml. 20 per cent glucose solution to form a paste. This paste was forced through screens having openings  $\frac{1}{16}$  inch in diameter. The extruded material was dried at 50°C. and broken into segments of average weight of 5 mgm. The tributylphosphate solution was prepared by dissolving 65 gm. of the carbamate in 123 ml. tributylphosphate. The solution was applied full strength for the 50-pound rate and was diluted with No. 2 Diesel oil for the 10-pound rate. These solutions were applied as sprays at a volume rate of 14 ml. per square yard. The aqueous solution was a saturated solution of the compound in water. This preparation was used only in the greenhouse experiments.

Persistence was determined by observations of emergence and plant response of common spring oats and U. S. No. 13 corn planted at weekly intervals. Metal flats, 15 by 19.5 inches, were used for greenhouse experiments, and plots, 5 by 9 feet, were used for field experiments.

In the experiment on rate of compound, finely powdered isopropyl N-phenyl carbamate was used at rates of 2, 10, 50, and 250 mgm. per pound of soil. At the three lowest rates, the compound was mixed with Fuller's earth in such proportions that the total amount of dust added per pound of soil was always 250 mgm. The dusts were thoroughly mixed with 35 pounds of air-dry Frankstown very fine sandy loam contained in 15 by 19.5-inch metal flats. The soil was watered as necessary. Soil temperature ranged from 20 to 33°C. and averaged about 23°C. Persistence was determined by observations of emergence and plant response of common spring oats planted at 3- to 5-day intervals.

In other experiments the isopropyl N-phenyl carbamate was added at a rate of 5 mgm. per pound of soil in a solution of such volume as to bring the soil moisture to the desired level, except that at 20 and 40 per cent of the water-holding capacity the soil was first brought up to 60 per cent of the water-holding capacity and then rapidly dried to the required level. The pots were covered during the incubation period, and water was added as required. At intervals, pots were dried with an electric fan, the soil was removed, thoroughly mixed, and planted to Vicland oats, common spring oats, or Wong barley.

Frankstown silt loam of pH 6.7 was used for most of the studies. For potting

use, this was mixed with sand in a ratio of 2 soil to 1 sand. In a few moisture level experiments and in the rate experiment Frankstown very fine sandy loam of pH 6.7 was used without admixture.

#### RESULTS AND DISCUSSION

The effect of soil temperature on the persistence of isopropyl N-phenyl carbamate was determined in one experiment. Soils containing this compound were incubated at 10, 15, 20, 25, and 30°C. at 60 per cent of the water-holding capacity and at intervals were planted to Vicland oats. In the planting made after 8 days' incubation at 10, 15, 20, 25, and 30°C., the emergence was 0, 40, 50, 80, and 100 per cent of the control, respectively. Emerging plants were stunted and the response was increasingly severe with decreasing temperature. After

TABLE 1  
*Persistence of isopropyl N-phenyl carbamate in soil at various moisture levels*  
Incubation temperature 25° C.

INCUBATION TIME	EMERGENCE* OF COMMON SPRING OATS					
	20% WHC†	40% WHC	60% WHC	80% WHC	100% WHC	Flooded soil
<i>days</i>						
3	0	0	0	0	0	0
6	0	0	0	0	0	0
9	2A‡	9A	1A	0	0	0
12	44A	77A	23A	36A	3A	0
15	41A	87A	53A	12A	29A	11A
19	97	96	95	93	64A	12A

\* In percentage of untreated controls.

† WHC = water-holding capacity of soil.

‡ A indicates abnormal plants.

20 days' incubation, the only effect was a slight stunting of the oat seedlings grown in soil incubated at 10°C. After 36 days' incubation, there was no visible response at any temperature.

Isopropyl N-phenyl carbamate disappeared equally rapidly at moisture contents from 20 to 80 per cent of the water-holding capacity (table 1). The plants that emerged from soil after 9, 12, or 15 days' incubation were stunted and in most instances probably would have died after a short growth period. After 19 days' incubation the compound had disappeared at all moisture levels except at 100 per cent of the water-holding capacity and from flooded soil. In three other experiments run at slightly higher temperatures, but not higher than 28°C., isopropyl N-phenyl carbamate disappeared within 3 weeks at all moisture levels.

The persistence of this carbamate was influenced by its rate of addition to soil. At rates of 2, 10, 50, and 250 mgm. per pound of soil (9, 44, 220, and 1,102 pounds per acre) the compound disappeared in 15, 19, 39, and 39 days, respec-

tively (table 2), as indicated by normal plant growth. Since this compound was nonpersistent even at these excessively high rates, there can be little danger from overtreatment in its use as a herbicide.

In another experiment the rate and form of isopropyl N-phenyl carbamate had no appreciable effect on its persistence under greenhouse conditions. The compound in all instances disappeared within 3 weeks. At the 50-pound rate there was, however, in general, a greater reduction in the percentage emergence than at the 10-pound rate. In field experiments there was an indication that the 50-pound rate persisted slightly longer than the 10-pound rate. Four weeks after treatment, at 10- and 50-pound rates, emergence of common spring oats was 80 and 55 per cent of the controls, respectively. Isopropyl N-phenyl carbamate applied as an oil spray at a rate of 10 pounds per acre had essentially

TABLE 2  
*Persistence of isopropyl N-phenyl carbamate applied to soil at four rates*

INCUBATION TIME  <i>days</i>	EMERGENCE* OF COMMON SPRING OATS			
	2 mgm.†	10 mgm.	50 mgm.	250 mgm.
0	0	0	0	0
5	0	0	0	0
8	43A‡	0	0	0
11	85A	0	0	0
15	127	48A	18A	0
19	90	92	52A	8A
36	103	111	3A	0
39	140	132	124	152
43	84	89	71	95

\* In percentage of untreated controls.

† mgm. of the carbamate per pound of soil.

‡ A indicates abnormal plants.

disappeared within 2 weeks after treatment, but applied in the other forms at the same rate it persisted 3 to more than 4 weeks.

When the soils were incubated at 60 per cent of the water-holding capacity and at 28°C., isopropyl N-phenyl carbamate persisted more than 9 weeks in autoclaved soils and less than 2 weeks in nonautoclaved soils. This experiment was terminated after 9 weeks, and at this time there was no evidence of decreased toxicity of the compound. These results along with the results on the effect of soil moisture and soil temperature are in accord with the view that the disappearance of this compound is due to the action of microorganisms.

The disappearance of isopropyl N-phenyl carbamate from soil is probably caused by its hydrolysis to form isopropyl alcohol and N-phenyl carbamic acid. The N-phenyl carbamic acid, which is extremely unstable, would be decarboxylated to form aniline. These products have little effect at the usual herbicidal concentrations on germination or emergence of oats. Aniline or isopropyl alcohol at rates of 5 and 20 mgm. per pound of soil and isopropyl alcohol at 50

mgm. had no noticeable effect on the emergence of common spring oats, whereas aniline at 50 mgm. had a slight retarding effect on emergence. This hypothetical breakdown probably could be accomplished by many soil microorganisms.

The disappearance of certain substituted phenoxyacetic acids from soils has been shown by DeRose and Newman (2) to be caused by microbial action. The disappearance of isopropyl N-phenyl carbamate is also due to microbial action, but it takes place more rapidly over a wide range of soil temperature and moisture conditions than does that of the phenoxyacetic acids. This rapid inactivation of isopropyl N-phenyl carbamate may prevent its employment for the control of grasses which germinate slowly.

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# EFFECT OF STRAW MULCH ON RECOVERY OF NITROGEN FROM NITRATE OF SODA AND AMMONIUM SULFATE APPLIED AS TOP-DRESSING

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## EXPERIMENTAL CONDITIONS

Sixteen of the lysimeters used in the mulch experiments with Cumberland loam and reported in the companion article—"Effects of Wheat Straw, Lespedeza Sericea Hay, and Farmyard Manure, as Soil Mulches, on the Conservation of Moisture and the Production of Nitrates"—were used in a supplemental project to determine the effects of the straw mulch on the recovery of nitrogen from nitrate of soda and from ammonium sulfate applied as top-dressing. The treatments tabulated were repetitions of those given three years before. Prior to placement of the mulch, the soil of each tank was taken up, thoroughly mixed, and replaced. The incorporated manure was mixed with the total amount of soil. As previously, the straw was chopped to approximately  $\frac{1}{4}$ - to 1-inch lengths and applied at the rate of 5 tons per acre. Nitrate of soda analyzing 15.9 per cent nitrogen, and ammonium sulfate analyzing 21.1 per cent, were top-dressed on the soil tanks at the rate of 50 pounds of nitrogen per acre for each material. Following the top-dressing,  $\frac{1}{2}$  inch of water was applied to the entire set, which was exposed to air conditions September 6, 1945. No further watering was given and no crop was grown.

Unlimed soil was used for the nitrate of soda series and limed soil for the ammonium sulfate series. Ground limestone had been applied several years earlier to the one series in sufficient quantity to produce, in 1946, a light surface growth of lichens with little moss, whereas moss predominated on the unlimed set. The average pH for the limed tanks was 6.67 and for the unlimed 5.53. The limed set was used for the ammonium sulfate applications because of the well-known fact that this material requires a nearly neutral soil to give the best fertilizer results through conversion to nitrate.

## RESULTS

Table 1 shows that at the end of the year full recovery of the applied nitrate had been obtained from the unmulched tanks, but that under the straw-mulch condition the average recovery was only 73.4 per cent. In the case of the ammonium sulfate, the unmulched tanks showed an average recovery of 65.6 per cent and the straw-mulched 51.0 per cent. The straw mulch obviously reduced the availability of the nitrogen in both carriers. At least for this soil type, nitrate of soda is suggested as the much superior form of fertilizer nitrogen for use under straw mulch. In fact, its judicious use appears warranted as a means of overcoming the detrimental effects of the straw mulch.

TABLE 1

*One-year leachates and recovery of nitrogen applied as nitrates of soda and ammonium sulfate*  
 Rate of application 50 pounds of nitrogen per acre, 1945-46

SERIES	TREATMENTS	LEACHATES	NITROGEN OBTAINED PER ACRE		
			Without fertilizer nitrogen	With nitrate of soda	Recovery of applied nitrogen
1. Unlimed		<i>kgm.</i>	<i>pounds</i>	<i>pounds</i>	<i>per cent</i>
	None.....	314.7	18.5	69.0	101.0
	Straw mulch.....	461.4	18.8	50.9	64.0
	Straw mulch and manure incorporated.....	459.1	69.1	110.3	82.4
	Manure incorporated.....	326.1	88.7	140.5	103.6
	Average.....	390.3	48.8	92.7	87.8
2. Limed				With ammonium sulfate	
	None.....	318.9	32.9	62.8	60.0
	Straw mulch.....	453.7	21.7	42.7	42.0
	Straw mulch and manure incorporated.....	455.6	79.0	108.9	60.0
	Manure incorporated.....	320.2	114.2	149.9	71.4
	Average.....	387.1	62.0	91.1	58.0

## Averages

TREATMENT	LIMED AND UNLIMED PERCOLATES	RECOVERY OF APPLIED NITROGEN	
		From nitrate of soda	From ammonium sulfate
	<i>kgm.</i>	<i>per cent</i>	<i>per cent</i>
Without straw mulch.....	320	102.4	65.6
With straw mulch.....	458	73.4	51.0

# MICROBIOLOGICAL DECOMPOSITION OF WATER HYACINTH

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The growth of water hyacinth (*Eichhornia crassipes*), which after every rainy season covers the lowlands, has become a serious menace to agriculture, fisheries, and health and sanitation of rural Bengal. All attempts to eradicate this pest have failed. The Bengal Department of Agriculture suggested the possibility of utilizing the plant as a source of manure to meet, to some extent, the deficiency of nitrogen in the soils of India and Pakistan. It does not appear, however, that any scientifically systematic work heretofore has been done in this direction.

The first step toward this attempt was obviously to obtain information regarding the course of decomposition of water hyacinth in compost and in soil. With this object in view, the present investigation was undertaken.

A considerable amount of work has been done on the decomposition of plant material in compost and in soil. Among the early workers, Boussingault (5) observed that the process of decomposition involves, primarily, absorption of oxygen and liberation of an approximately equal volume of carbon dioxide. The conditions that control the course of such decomposition have been worked out by Omeliansky (16), Hebert (8), Hope-Seyler (10), and more recently by Waksman and his co-workers (19, 20, 22, 23, 24, 25, 26, 27, 28) and by Page and his co-workers (9, 17). Hutchinson and Richards (11), in their work on the production of artificial manure from vegetable materials, recognized that simple nitrogenous substances are essential for the decomposition and determined the quantity necessary for satisfactory rotting under aerobic conditions. Waksman and his co-workers showed clearly that ammonia is set free if the nitrogen content of the medium is high, and if it is low, decomposition is retarded, or is hastened only by adding inorganic nitrogen salts up to a concentration of 1.7–1.8 per cent of the material. Acharya (1, 2, 3) showed that much less nitrogen is required under anaerobic conditions than under aerobic conditions.

As to the decomposition of the different constituents of the plant materials, it has been observed that water-soluble materials are utilized with the greatest speed, followed by hemicellulose and pentosans, then by cellulose, the lignin being the most resistant fraction (8, 14, 18, 19, 20, 24, 25, 26, 27, 28).

Other studies have shown that the rate of decomposition of plant materials is greatest under aerobic conditions, intermediate under waterlogged conditions, and least under anaerobic conditions (1, 2, 3, 7, 25).

<sup>1</sup> The author expresses his appreciation to P. K. De, M. Sulaiman, and S. S. Guha Sarkar, for their constructive criticisms during the progress of this work.

## DECOMPOSITION IN COMPOST

*Materials and methods*

Water hyacinth used in this investigation was collected from a local field and dried in the sun. The sun-dried materials were chafed to pieces, dried at 105° C., and powdered. The powder was then analyzed for the following constituents:

1. Fats and waxes—by extraction with alcohol and benzene mixture (1:1).
2. Total furfural—by the standard method of Krobber and Tollens (4, pp. 344-345).
3. Cellulose—by the method suggested by Chattopadhyay and Sarker (6).
4. Lignin—by the process suggested by Norman and Jenkins (15).
5. Protein—by determining total nitrogen by the standard Kjeldahl method and multiplying by the factor 6.25.
6. Organic carbon—by the rapid titration procedure devised by Walkley (29).

The results, on an oven-dry basis, were as follows: fats and waxes, 1.9 per cent; furfural, 7.7 per cent; cellulose, 40.0 per cent; lignin, 16.0 per cent; protein, 10.7 per cent; organic carbon, 43.2 per cent; C/N ratio, 25.26.

Ten-gram portions of the chafed material were distributed in 250-ml. Erlenmeyer flasks to which the following treatments were applied, each treatment being replicated six times: distilled water only (control); water plus  $(\text{NH}_4)_2\text{SO}_4$ ; water plus  $(\text{NH}_4)_2\text{SO}_4$  and 0.01 gm.  $\text{CaCO}_3$ ; water plus  $\text{NH}_4\text{NO}_3$ ; and water plus  $\text{NaNO}_3$ .

Nitrogen was supplied by adding calculated volumes of standard solutions of the different compounds to supply 0.05 gm. nitrogen to each flask.

For the introduction of inoculum, a suspension of an old well-rotted manure in water was prepared, and after the heavier particles had settled, a 1-ml. portion was added to each flask. The materials were then thoroughly moistened by spraying with the jet of a wash bottle, care being taken to avoid waterlogging.

For aerobic decomposition, flasks were plugged with cotton wool and kept at room temperature, each flask being vigorously shaken daily to facilitate aeration and even distribution of moisture.

For anaerobic decomposition, each flask was fitted with a rubber stopper carrying two glass tubes bent at right angles. The flasks were then joined in series by connecting the glass tubes of adjacent flasks with rubber tubing, one tube at each end being left free. One of these tubes served as an outlet; and through the other, carbon dioxide was passed from a Kipp's apparatus for 1 hour daily.

At appropriate regular intervals one flask from each treatment was removed and its contents were carefully taken out and dried at 105° C. The dried mass was weighed and finely powdered, and small portions were used for the determination of different constituents.

*Results*

There was an abundant growth of fungus in all the aerobic flasks during the early period of decomposition. A network of mycelia was observed over the surface of the materials every day. During shaking of the flasks, these mycelia broke down, but a new growth appeared on the following day. This growth, however, disappeared toward the latter part of the experiment.



The chafed material, which at the start nearly filled the flasks, gradually became reduced in volume and turned deep brown with a black tinge. A foul odor was given off. Toward the latter part of the experiment, when decomposition had advanced to a considerable degree, water separated from the decomposing material, forming a thin layer over the bottom of the flask. This was because cellulosic materials, which absorbed large volumes of water at the start, lost that power after decomposition, resulting in liberation of the absorbed water.

In the anaerobic series, no fungal growth was noticed. This was to be expected in view of the fact that these organisms are strictly aerobic. The material showed no marked reduction in volume, and although it turned brown in the course of decomposition, the color was not so deep as in the aerobic experiment. The odor evolved was far more offensive than that in the aerobic experiment.

The effects of different treatments on the degree of decomposition of water hyacinth as a whole and of its different constituents are shown in tables 1 to 5. The percentages left after 90 days' decomposition are given in table 6 for comparison.

Loss of dry matter was much greater under aerobic conditions than under anaerobic conditions. As is shown later in this paper, fungi are more active than bacteria in the decomposition of water hyacinth in soil. The inability of fungi to grow in the anaerobic flasks probably accounts for the slow decomposition under this condition. Guha Sarkar, De, and Bhowmick (7), who studied the decomposition of rice straw, also observed that anaerobic decomposition was slower than aerobic. They sought to explain this phenomenon by the accumulation, under anaerobic conditions, of organic acids formed as a result of incomplete fermentation of carbohydrates, resulting in a lowering of pH which prevents further microbial growth.

As shown in table 6, more than 50 per cent of the dry matter disappeared in 90 days under aerobic conditions even when no nitrogen was added. Addition of nitrogen in different forms undoubtedly accelerated decomposition, but by the end of 90 days only about 10 per cent more material had been decomposed than without nitrogen. For example, maximum decomposition took place with  $\text{NaNO}_3$ , in which case 63 per cent of the dry matter was lost as against 52 per cent without addition of nitrogen. This shows that the nitrogen present in water hyacinth or liberated from it in available form was just sufficient to satisfy the need of the microorganisms that took part in the decomposition. The percentage of nitrogen in the sample of water hyacinth used in the experiment was 1.71. Waksman and Tenney (24) have shown that plant materials containing 1.7 per cent or more of nitrogen will undergo rapid decomposition without addition of extra nitrogen. Guha Sarkar, De, and Bhowmick (7) have observed that for successful aerobic fermentation of rice straw, a material poor in nitrogen, 1.7 to 1.9 per cent nitrogen is necessary. The rapid decomposition of water hyacinth, as observed in this experiment, was thus in agreement with the observation of previous workers.

The effects of the different forms of nitrogen compounds on the degree of decomposition, arranged in order of increasing efficiency, were as follows:



$(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ . It was found that sodium nitrate accelerated the decomposition not only of dry matter as a whole but also of the individual

TABLE 1

*Decomposition of water hyacinth under aerobic and anaerobic conditions in absence of added nitrogen*

Oven-dry basis

CONSTITUENTS	AT START	AFTER DECOM- POSING 15 DAYS		AFTER DECOM- POSING 30 DAYS		AFTER DECOM- POSING 45 DAYS	AFTER DECOM- POSING 60 DAYS		AFTER DECOM- POSING 75 DAYS	AFTER DECOM- POSING 90 DAYS	
		Aero- bic	Anae- robic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Dry matter.....	8.65	7.50	8.10	6.83	7.85	6.15	5.19	7.31	4.40	4.20	7.22
Protein.....	0.92	0.84	0.77	0.74	0.69	0.77	0.73	0.56	0.69	0.67	0.54
Furfural.....	0.67	0.47	0.63	0.41	0.61	0.35	0.30	0.53	0.27	0.24	0.52
Cellulose.....	3.46	2.55	3.29	2.20	3.19	1.83	1.51	2.98	1.25	1.07	2.96
Lignin.....	1.38	1.37	1.37	1.36	1.37	1.32	1.30	1.36	1.26	1.25	1.36
Fats and waxes.	0.16	0.11	0.15	0.09	0.14	0.08	0.07	0.14	0.06	0.06	0.13
N.....per cent	1.71	1.79	1.53	1.85	1.25	1.99	2.18	1.21	2.52	2.54	1.20
C.....per cent	43.20	....	....	43.30	42.20	....	45.91	43.00	....	47.80	43.01
C/N ratio.....	25.26	....	....	23.40	33.70	....	21.05	35.50	....	18.81	35.84

TABLE 2

*Decomposition of water hyacinth under aerobic and anaerobic conditions in presence of added ammonium sulfate*

Oven-dry basis

CONSTITUENTS	AT START	AFTER DECOM- POSING 15 DAYS		AFTER DECOM- POSING 30 DAYS		AFTER DECOM- POSING 45 DAYS	AFTER DECOM- POSING 60 DAYS		AFTER DECOM- POSING 75 DAYS	AFTER DECOM- POSING 90 DAYS	
		Aero- bic	Anae- robic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Dry matter.....	8.65	7.25	8.00	6.09	7.70	5.28	4.59	7.20	3.99	3.79	7.20
Protein.....	0.92	0.83	0.79	0.80	0.74	0.76	0.71	0.65	0.68	0.67	0.65
Furfural.....	0.67	0.43	0.62	0.33	0.60	0.29	0.27	0.55	0.25	0.23	0.55
Cellulose.....	3.46	2.39	3.18	1.81	3.08	1.45	1.18	2.91	0.97	0.90	2.91
Lignin.....	1.38	1.32	1.37	1.23	1.36	1.18	1.12	1.35	1.08	1.05	1.35
Fats and waxes.	0.16	0.10	0.15	0.08	0.13	0.06	0.05	0.12	0.04	0.04	0.12
N.....per cent	1.71	1.85	1.58	2.11	1.54	2.30	2.48	1.44	2.72	2.81	1.44
C.....per cent	43.20	....	....	40.83	43.49	....	44.10	44.30	....	46.57	44.19
C/N ratio.....	25.26	....	....	19.35	28.27	....	17.82	30.81	....	16.57	30.73

constituents. According to Guha Sarkar *et al.* (7), the effect of sodium nitrate is due to its oxidizing action and also to the greater solubility of lignin in alkali,

formed as a result of absorption of the nitrate ion by microorganisms, leaving behind the sodium ion, which formed sodium hydroxide with water.

TABLE 3

*Decomposition of water hyacinth under aerobic and anaerobic conditions in presence of added ammonium sulfate and calcium carbonate*

Oven-dry basis

CONSTITUENTS	AT START	AFTER DECOM- POSING 15 DAYS		AFTER DECOM- POSING 30 DAYS		AFTER DECOM- POSING 45 DAYS	AFTER DECOM- POSING 60 DAYS		AFTER DECOM- POSING 75 DAYS	AFTER DECOM- POSING 90 DAYS	
		Aero- bic	Anae- robic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Dry matter.....	8.65	7.35	7.80	6.15	7.45	5.45	4.65	6.82	4.00	3.82	6.59
Protein.....	0.92	0.85	0.78	0.77	0.72	0.74	0.07	0.64	0.66	0.64	0.61
Furfural.....	0.67	0.46	0.60	0.33	0.57	0.31	0.27	0.54	0.24	0.23	0.53
Cellulose.....	3.46	2.46	3.09	1.83	2.91	1.56	1.15	2.63	0.97	0.91	2.64
Lignin.....	1.38	1.33	1.35	1.25	1.33	1.16	1.11	1.32	1.07	1.05	1.31
Fats and waxes.	0.16	0.11	0.14	0.08	0.13	0.07	0.06	0.12	0.04	0.04	0.11
N..... per cent	1.71	1.85	1.60	2.00	1.55	2.18	2.39	1.49	2.63	2.68	1.47
C..... per cent	43.20	....	....	40.50	43.40	....	43.02	44.30	....	46.07	45.10
C/N ratio.....	25.26	....	....	20.25	27.90	....	18.00	29.60	....	17.18	30.70

TABLE 4

*Decomposition of water hyacinth under aerobic and anaerobic conditions in presence of added ammonium nitrate*

Oven-dry basis

CONSTITUENTS	AT START	AFTER DECOM- POSING 15 DAYS		AFTER DECOM- POSING 30 DAYS		AFTER DECOM- POSING 45 DAYS	AFTER DECOM- POSING 60 DAYS		AFTER DECOM- POSING 75 DAYS	AFTER DECOM- POSING 90 DAYS	
		Aero- bic	Anae- robic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Dry matter.....	8.65	6.92	7.50	5.66	6.80	4.99	4.39	6.06	3.82	3.46	5.60
Protein.....	0.92	0.83	0.74	0.78	0.65	0.73	0.68	0.57	0.64	0.62	0.52
Furfural.....	0.67	0.41	0.58	0.32	0.55	0.28	0.25	0.51	0.23	0.21	0.47
Cellulose.....	3.46	2.26	2.77	1.73	2.50	1.35	1.12	2.28	0.10	0.08	2.11
Lignin.....	1.38	1.28	1.32	1.19	1.28	1.16	1.14	1.25	1.11	1.06	1.23
Fats and waxes.	0.16	0.09	0.12	0.07	0.11	0.07	0.06	0.10	0.05	0.04	0.09
N..... per cent	1.71	1.91	1.58	2.20	1.53	2.34	2.46	1.52	2.68	2.88	1.48
C..... per cent	43.20	....	....	44.00	43.00	....	45.20	44.40	....	47.20	45.00
C/N ratio.....	25.26	....	....	20.00	28.06	....	18.37	29.28	....	16.38	30.36

Of the individual constituents, cellulose apparently underwent the greatest decomposition. At the end of 90 days the amount decomposed in the absence

of added nitrogen represented 70 per cent of that originally present, which was about 55 per cent of the total loss of dry matter during the period. With sodium nitrate, the corresponding loss was 80 per cent of the original, amounting to 50 per cent of the total loss of organic matter. The results in tables 1 to 5 further show that the rate of decomposition was most rapid during the first 15 days, after

TABLE 5

*Decomposition of water hyacinth under aerobic and anaerobic conditions in presence of added sodium nitrate*

Oven-dry basis

CONSTITUENTS	AT START	AFTER DECOM- POSING 15 DAYS		AFTER DECOM- POSING 30 DAYS		AFTER DECOM- POSING 45 DAYS	AFTER DECOM- POSING 60 DAYS		AFTER DECOM- POSING 75 DAYS	AFTER DECOM- POSING 90 DAYS	
		Aero- bic	Anae- robic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic	Aerobic	Aero- bic	Anae- robic
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Dry matter.....	8.65	6.65	7.10	5.45	6.30	4.65	4.00	5.60	3.40	3.20	5.19
Protein.....	0.92	0.79	0.69	0.74	0.59	0.70	0.66	0.52	0.61	0.59	0.48
Furfural.....	0.67	0.37	0.57	0.30	0.52	0.27	0.24	0.48	0.21	0.19	0.45
Cellulose.....	3.46	2.08	2.63	1.56	2.28	1.15	0.94	2.08	0.80	0.69	1.91
Lignin.....	1.38	1.25	1.29	1.16	1.25	1.11	1.07	1.21	1.03	0.99	1.18
Fats and waxes.	0.16	0.08	0.12	0.07	0.10	0.06	0.06	0.09	0.05	0.04	0.09
N.....per cent	1.71	1.90	1.56	2.18	1.49	2.39	2.63	1.48	2.87	2.95	1.48
C.....per cent	43.20	....	....	43.62	43.30	....	45.70	44.48	....	47.44	44.88
C/N ratio.....	25.26	....	....	20.00	29.00	....	17.30	30.00	....	16.08	30.34

TABLE 6

*Percentages of original constituents of water hyacinth left after 90 days of decomposition*  
Oven-dry basis

TREATMENT	DRY MATTER		PROTEIN		FURFURAL		CELLULOSE		LIGNIN	
	Aerobic	Anae- robic	Aerobic	Anae- robic	Aerobic	Anae- robic	Aero- bic	Anae- robic	Aero- bic	Anae- robic
Control.....	48.5	83.5	72.6	58.6	36.2	78.2	30.9	85.4	90.0	98.0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	43.9	83.2	72.0	70.2	35.0	83.2	26.0	84.2	76.2	97.4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + CaCO <sub>3</sub> ....	44.2	76.2	70.4	65.5	34.2	79.1	26.2	76.3	76.2	94.9
NH <sub>4</sub> NO <sub>3</sub> .....	40.0	64.7	67.5	56.1	31.3	70.2	23.8	60.9	76.9	89.0
NaNO <sub>3</sub> .....	37.0	60.0	63.8	51.9	28.0	66.9	20.0	55.1	72.0	85.2

which it decreased considerably. Thus in the absence of added nitrogen, 27 per cent of the total 70 per cent loss took place in the first 15 days. In the presence of sodium nitrate, the loss during this period was 40 per cent out of a total loss of 80 per cent. It appears, therefore, that the most important feature in the decomposition of water hyacinth is the rapid loss of cellulose, which accounts for the major part of the organic matter lost. This is quite in agreement with the observation of Waksman (23), Waksman and Tenney (24), Norman (13), and

Guha Sarkar *et al.* (7), all of whom observed rapid loss of cellulose from the plant materials with which they worked.

Furfural, which is mainly derived from the pentose units of hemicellulose and the xylan associated with cellulose, represented only 7.7 per cent of the dry matter. These substances decomposed rapidly, the amounts found at the end of 90 days being 36 and 28 per cent of the original with no nitrogen and with sodium nitrate respectively. Here again the decomposition was most rapid within the first 15 days. During this period the loss was 30 per cent of a total loss of 64 per cent with no added nitrogen, and 45 per cent of a total loss of 72 per cent with sodium nitrate. Norman (13) observed that during the decomposition of oat and rye straw, there was a definite, though slight, increase in the furfural after an initial rapid fall. This he ascribed to the formation of intermediate products capable of forming furfural under certain conditions. No such evidence is afforded by the results of the present experiment, which show a progressive fall of furfural.

The resistance of lignin to microbiological attack is a common observation. Only 10 per cent of the amount originally present was lost when no nitrogen was added. In presence of added nitrogen the decomposition was greater, but even then as much as 72 per cent of the original was left even under the most favorable conditions for decomposition. Rege (18) and Norman (13) were of the opinion that lignin is an inhibitory factor in decomposition, because by providing a resistant barrier to the growth of many microorganisms it reduces the strength of the general attack on the more available constituents.

There was a progressive increase in the percentage of nitrogen in the materials left after aerobic decomposition. This is obviously due to the fact that the non-nitrogenous constituents decomposed at a much greater rate than the nitrogenous constituents, with the result that the materials left after decomposition became rich in nitrogen. It will be found, however, that although the percentage of nitrogen gradually increased, the total protein content slowly decreased with the progress of decomposition. The results thus show that some nitrogen was lost in course of decomposition of water hyacinth under both aerobic and anaerobic conditions.

A comparison of the composition of water hyacinth compost with that of horse manure (table 7) indicates the manurial value of the former. The main difference in the composition of the two manures lies in the higher cellulose and lower hemicellulose contents of water hyacinth compost. The sum of these two constituents, which represent the total source of energy, is nearly the same in both cases, however, showing thereby that the decomposition will not be very different. It is presumed, therefore, that water hyacinth manure will be equally as effective for plant growth as is horse manure.

#### DECOMPOSITION IN SOIL

Since water hyacinth composted under controlled conditions was found to give a product of high manurial efficiency, the next step was to investigate its decomposition in the soil and to determine its effect on the nitrogen contents and microbial population of the soil.



*Effect of decomposition on nitrogen content of soil*

Two soils, one from Dacca farm (pH 5.4) and the other from Faridpur (pH 8.35), were air-dried, and 700-gm. portions of each were distributed to three large glass troughs, one of which was left untreated as a control, while the other two were respectively treated with 7.0 gm. of stem powder and 3.50 gm. of leaf powder. After the added materials were thoroughly mixed with the soil, the moisture content was adjusted to 15 per cent on a dry basis. To maintain the water content at this level, the weights of the containers were taken at the start

TABLE 7

*Composition of horse manure in comparison with that of water-hyacinth compost prepared under aerobic conditions with and without added nitrogen*

CONSTITUENTS	HORSE MANURE	WATER HYACINTH WITHOUT N	WATER HYACINTH + NaNO <sub>3</sub>
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Fats and waxes.....	1.1	1.3	1.23
Hemicellulose.....	13.02	5.7	5.8
Cellulose.....	15.59	25.4	21.63
Lignin.....	27.02	29.7	31.07
Total N.....	2.35	2.54	2.95
C/N.....	.....	18.8	16.08

TABLE 8

*Changes in total nitrogen content of soil as affected by decomposition of water hyacinth  
Oven-dry basis*

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
		<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Dacca, pH 5.4	Control	1,427.7	1,440.3	1,451.2	1,440.2	1,431.3
	Stem	1,572.4	1,581.4	1,580.1	1,582.8	1,577.4
	Leaf	1,597.4	1,601.4	1,610.1	1,597.3	1,599.3
Faridpur, pH 8.35	Control	595.0	600.1	602.2	589.2	592.4
	Stem	740.2	744.8	747.0	730.4	736.4
	Leaf	746.3	746.3	748.3	740.3	742.2

and the loss due to evaporation was replaced by periodic additions of water. On the day of analysis, moisture was adjusted and representative samples were withdrawn; the dishes were then reweighed, and these weights were maintained until the next sampling.

At 15-day intervals, samples were withdrawn and analyzed for total, ammoniacal, and nitrate nitrogen. Nitrogen was estimated by the routine Kjeldahl method; ammonia by leaching the soil (40 gm.) with *N* KCl solution (400 ml.) and distilling the leachate with magnesium oxide; and nitrate by distilling the residue left after ammonia estimation with Devarda's alloy. The results are shown in tables 8, 9, and 10.



The results in table 8 show that the total nitrogen contents of the soils remained virtually constant, regardless of treatment. These results are different from those of the compost experiments, in which considerable loss of nitrogen was observed. This discrepancy in results suggests that decomposition of water hyacinth in soil did not follow the same course as in compost.

The ammonia contents of the soils (table 9) increased progressively until the 45th day, after which they began to fall. In control Dacca soil, the ammonia contents increased from 19.5 p.p.m. at the start to 45.5 p.p.m. on the 45th day, but during the same period the ammonia contents in the stem and leaf treatments rose to 87.1 and 79.4 p.p.m. respectively. In Faridpur soil, the accumulation of ammonia was much less than in Dacca soil. This was obviously not due to volatilization of part of the ammonia formed, as might be supposed on account of the alkaline reaction of the soil (pH 8.3). The lack of change in total nitrogen content of the soil shows that no loss of nitrogen in any form

TABLE 9

*Changes in ammonical nitrogen content of soil as affected by decomposition of water hyacinth*  
Oven-dry basis

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
		<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Dacca, pH 5.4	Control	19.5	28.7	39.7	45.5	40.2
	Stem	....	45.8	72.0	87.1	79.4
	Leaf	....	49.1	70.3	79.4	67.4
Faridpur, pH 8.35	Control	5.7	8.8	10.9	14.4	10.4
	Stem	....	8.0	22.4	38.3	29.9
	Leaf	....	8.4	20.3	35.3	24.4

took place. In Faridpur soil, the ammonia content rose from 5.7 p.p.m. to 14.4 p.p.m. on the 45th day in the control and to 38.3 p.p.m. and 35.3 p.p.m. respectively in the stem and leaf treatments. As in Dacca soil, the stem liberated more ammonia than the leaf.

The results, on the whole, show that part of the nitrogen of water hyacinth becomes readily available in soil and that the nitrogen of the stem is slightly more available than that of the leaf. The accumulation of more ammonia in Dacca soil, as compared with that in Faridpur soil, suggests that conditions prevailing in the former were more favorable for decomposition of water hyacinth. That decomposition took place more rapidly in Dacca soil is further substantiated by the fact that maximum accumulation of ammonia took place between the 15th and the 30th day, whereas in Faridpur soil it took place between the 30th and the 45th day.

The changes in nitrate (table 10) followed a course quite opposite to that of ammonia. From the start, the nitrate content slowly decreased until the 45th day, after which it increased. The loss was greater in the treated soils than in the controls. The nitrate contents of the control soils were thus greater than

those of the treated soils almost throughout the experiment. In view of the fact that the treated soils received additional amounts of nitrogen from the material added and that this nitrogen is rapidly ammonifiable, as found in the previous experiment, it was rather expected that the treated soils would contain much more nitrate than the controls. This discrepancy is probably due to the fact that a part of the nitrate originally present was assimilated by microorganisms at the expense of the energy materials added with water hyacinth and thus was converted into bacterial protoplasm.

The most remarkable feature of these results is that although large quantities of ammonia formed and accumulated, particularly in the treated soils, the nitrate contents remained at a low level and showed no increase whatever until after 45 days. Under normal conditions, the nitrate contents of soils are much greater than the ammonia contents, because of transformation of the latter to the former. The present results thus show that the conditions obtaining in the treated soils

TABLE 10

*Changes in nitrate nitrogen content of soil as affected by decomposition of water hyacinth*  
Oven-dry basis

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
		<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Dacca, pH 5.4	Control	35.3	32.1	31.8	30.0	33.7
	Stem	....	32.1	24.9	20.0	30.3
	Leaf	....	29.6	25.2	20.2	31.1
Faridpur, pH 8.35	Control	12.0	11.2	7.8	7.7	10.3
	Stem	....	8.4	5.1	2.0	10.9
	Leaf	....	8.0	6.3	3.3	12.0

were not favorable for nitrification during the first 45 days. Whether this was due to formation of material toxic to the nitrifying bacteria or to some other cause, however, is not known. After 45 days, the nitrate content showed an increase in all the soils, and this was marked by a simultaneous decrease, to almost the same degree, in ammonia contents. It appears, therefore, that after an initial lag of 45 days, the conditions became favorable for nitrification.

The results, summarized, indicate that considerable amounts of ammonia were formed in soils following application of water hyacinth, indicating that the plant material is suitable for use as a nitrogenous fertilizer. It was observed, however, that the ammonia accumulated in the soil for a long time without undergoing nitrification. This does not reduce the value of the water hyacinth as a fertilizer because, for most agricultural crops, ammonia is as good a nutrient as nitrate. On the other hand, accumulation of nitrate in soil has the disadvantage that it may be washed out or otherwise lost after a heavy shower. The absence of nitrate formation may therefore be regarded as an advantage rather than a disadvantage of water-hyacinth addition.

*Effect of decomposition on numbers of bacteria, fungi, and azotobacter*

As the transformation of added organic matter is chiefly due to activities of the microorganic population of soil, a study was next made of the changes in numbers of bacteria, fungi, and azotobacter with the progress of decomposition of water hyacinth. The experimental procedure was the same as in the previous experiment except that the leaf and stem powders were added together in the same troughs, in the proportion of 1 gm. of the mixture (stem: leaf, 2:1), per 100 gm. of soil. The methods of determining numbers of microorganisms were as follows:

*Bacteria.* Bacteria were counted by plate method using Thornton's (21) mannite agar medium ( $K_2HPO_4$ , 1.0 gm.;  $MgSO_4$ , 0.2 gm.;  $CaCl_2$ , 0.1 gm.;  $NaCl$ , 0.1 gm.;  $FeCl_3$ , 0.1 gm.;  $KNO_3$ , 0.5 gm.; mannite, 1.0 gm.; asparagine, 0.5 gm.; agar, 15 gm.;  $H_2O$ , 1,000 ml.). In preliminary trials, it was found that final soil dilutions of 1:10,000 and 1:20,000 were most suitable for counting bacteria in the Dacca and Faridpur soils respectively. The dilution adopted for Dacca soil, which has a pH of 5.4, was designed to rid the plates of fungal colonies, which, however, appeared even at this dilution. For each count, four parallel plates were used with an incubation period of 7 days at 27-28°C., a 1-ml. portion of the suspension being used in each plate.

*Fungi.* Fungi also were determined by plate method using a glucose-peptone medium ( $KH_2PO_4$ , 1 gm.;  $MgSO_4$ , 0.5 gm.; peptone, 5 gm.; glucose, 10 gm.; agar, 25 gm.;  $H_2O$ , 1,000 ml.). The pH of the medium was brought to 4 by addition of sulfuric acid. The dilutions employed here were 1:1,000 and 1:10,000 for the Faridpur and the Dacca soil respectively. The dilution employed for Dacca soil was for convenience in counting the enormously high numbers of colonies. The incubation period was nearly 60 hours, and four parallel plates were used for each count, a 1-ml. portion of the soil suspension being added to each plate.

*Azotobacter.* Azotobacter count was taken by the plate method using Jensen's (12) dextrin-agar medium ( $K_2HPO_4$ , 0.5 gm.;  $MgSO_4$ , 0.2 gm.;  $NaMoO_4$ , 0.025 gm.;  $FeCl_3$ , 0.05 gm.;  $CaCO_3$ , 5 gm.; dextrin, 10 gm.; agar, 20 gm.; distilled water, 1,000 ml.). In view of the acid reaction of Dacca soil, which does not allow growth of azobacter colonies, this soil was replaced by Sabour soil from Bihar with a pH of 8.30. The dilutions employed were 1:10 in Sabour soil and 1:5 in Faridpur soil, the latter being selected because of the very small number of colonies in this soil. For counting azotobacter, 0.2-ml. portions of the suspension were spread evenly with L-shaped glass rods on three parallel sterilized petri dishes containing the hardened dextrin-agar medium. The excess water was allowed to evaporate. The plates were incubated for 5 days at 27-28°C. The colonies, which developed as discrete, readily distinguishable white outgrowths, gradually turning black, were then counted.

The results are given in tables 11, 12, and 13.

The results in tables 11 and 12 show that bacteria and fungi multiplied rapidly in the soils, the increase being considerably greater in the treated soils than in the controls. Fungal counts were consistently higher in Dacca soil than in Faridpur soil, whereas the reverse was true of bacterial numbers. This was obviously due to the acid reaction of Dacca soil, which is known to favor fungal growth, and the alkaline reaction of Faridpur soil, which favors bacterial growth.

It will be recalled that ammonia accumulation was much greater in Dacca soil than in Faridpur soil, which suggested more complete decomposition of water hyacinth in the former. This fact, when considered along with the present observation that Dacca soil gave much higher fungal counts, would suggest that

the decomposition of water hyacinth in soils is carried out largely by fungi. The much greater decomposition of water hyacinth found in composts under aerobic conditions than under anaerobic conditions, where fungi are inactive, lends support to this idea.

Unlike bacteria and fungi, azotobacter were less abundant in the treated soils than in the controls (table 13). This was to be expected in view of the greater accumulation of ammonia in the treated soils. This observation is quite in line with the fact that addition of ammonium salts, nitrate, or materials rich in nitrogen tends to check the growth of azotobacter. This was shown by Zeimiecka (30), who determined the numbers of azotobacter in soils of the classical plots

TABLE 11

*Effect of addition of water hyacinth on bacterial numbers in soil*  
In millions per gram oven-dry soil, average of four plates

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
Dacca, pH 5.4	Control	1.2	2.1	9.9	14.2	20.5
	Stem and leaf	1.2	6.8	20.5	33.2	47.9
Faridpur, pH 8.35	Control	7.2	23.2	117.7	187.6	322.1
	Stem and leaf	7.2	93.2	222.1	310.8	461.5

TABLE 12

*Effect of addition of water hyacinth on fungal numbers in soil*  
In thousands per gram oven-dry soil, average of four plates

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
Dacca, pH 5.4	Control	818.4	1,740	3,468	6,149	7,425
	Stem and leaf	818.4	4,167	7,052	10,400	12,320
Faridpur, pH 8.35	Control	13.3	30.2	46.6	64.1	69.8
	Stem and leaf	13.3	146.9	209.3	256.9	285.5

at Rothamsted and found the highest number of colonies in plots receiving complete minerals except nitrogen, while plots receiving nitrogen showed no or few colonies of azotobacter. This was said to be due to the competition of azotobacter with other organisms, the growth of which was stimulated by the added nitrogen and which consequently outnumbered the azotobacter.

*Nitrogen fixation in a nitrogen-free culture solution containing water hyacinth as energy material*

To determine the value of water hyacinth as a source of energy material for azotobacter, the following water culture experiment was performed.

A culture solution was made up of 5 gm.  $K_2HPO_4$ , 0.2 gm.  $MgSO_4$ , 0.1 gm.  $NaCl$ , 0.1 gm.  $CaCl_2$ , 5 gm.  $CaCO_3$ , and 1,000 ml.  $H_2O$ . Of this, 100-ml. portions were placed in a number of 250-ml. Erlenmeyer flasks, to each of which



was added 1 gm. of leaf powder to form one series or 1 gm. of stem powder to form another series. Then into each of the flasks in both series was introduced 1 gm. of an inoculum of Sabour soil, which is known to contain a rather large number of azotobacter. Total nitrogen in the different cultures was determined at 20-day intervals.

The results in table 14 show that there was no noteworthy change in the total nitrogen content of the culture solutions. Despite its high cellulose content (40 per cent), water hyacinth, therefore, does not provide suitable energy material for azotobacter. This fact further substantiates the belief, previously expressed, that water hyacinth does not encourage the growth of azotobacter, but rather depresses it.

TABLE 13

*Effect of addition of water hyacinth on azotobacter numbers in soil*  
Numbers per gram dry soil, average of three plates

SOIL	TREATMENT	AT START	AFTER 15 DAYS	AFTER 30 DAYS	AFTER 45 DAYS	AFTER 60 DAYS
Sabour, pH 8.30	Control	2,130	2,575	2,353	3,513	3,639
	Stem and leaf	2,130	2,289	2,902	3,049	3,170
Faridpur, pH 8.35	Control	51	29	29	73	87
	Stem and leaf	51	15	0	0	15

TABLE 14

*Nitrogen fixation in culture solution with water hyacinth as energy source*  
Nitrogen in milligrams per 100 ml. of solution, average of duplicates

SOURCE OF ENERGY	AT START	AFTER 20 DAYS	AFTER 40 DAYS	AFTER 60 DAYS
Leaf .....	46.48	48.44	46.02	45.45
Stem .....	23.73	24.43	23.45	23.07

## SUMMARY

A study was made to determine the possible value of water hyacinth (*Eichhornia crassipes*), a prolific pest of the Bengal lowlands, as a source of manure to supply much-needed nitrogen to the soils of India and Pakistan.

A preliminary investigation was made of the decomposition of water hyacinth in compost under aerobic and anaerobic conditions with and without added nitrogen. The course of decomposition was followed by determining the loss of total dry matter, fats, furfural, cellulose, lignin, and protein.

The decomposition of organic matter as a whole and of different constituents (except proteins) was much greater under aerobic than under anaerobic conditions.

About 50 per cent of the total organic matter disappeared in 90 days under aerobic conditions even when no nitrogen was added. Addition of different forms of nitrogen accelerated decomposition, but at the end of 90 days only 10



per cent more material had decomposed than without nitrogen. The different forms of nitrogen, arranged in order of increasing efficiency, are as follows:  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ .

Of the plant constituents, cellulose underwent the greatest decomposition, accounting for about 50 per cent of the total loss of dry matter. The rate of loss was most rapid within the first 15 days, after which it slowed considerably.

Furfural-yielding substances decomposed as rapidly and almost to the same degree as cellulose. There was no evidence of the formation of intermediate compounds capable of yielding furfural under conditions of decomposition.

The loss of lignin was only 10 per cent of the original when no nitrogen was added; with  $\text{NaNO}_3$ , it was 23 per cent.

The percentage of total nitrogen of the materials left after decomposition, progressively increased, showing that the nonnitrogenous constituents were disappearing much more rapidly than the nitrogenous. The total protein contents, however, gradually diminished with decomposition of the materials, showing that some loss of nitrogen took place.

A comparison of water-hyacinth compost with horse manure indicated almost equal manurial efficiency of the two.

In view of the encouraging results of the preliminary study, a further investigation was made of the decomposition of water hyacinth in soil and its effect on the total, ammoniacal, and nitrate nitrogen contents as well as on the fungal, bacterial, and azotobacter numbers.

The total nitrogen content showed virtually no loss during decomposition of the plant in the two soils studied: Dacca (pH 5.4) and Faridpur (pH 8.35). The ammonia content rapidly increased in both soils, the increase being relatively greater in the Dacca than in the Faridpur soil, and remained at a high level until the 45th day, after which signs of nitrification appeared.

Both bacterial and fungal numbers rose markedly in the control as well as in the treated soils, the rise being considerably higher in the latter. Fungal numbers were much higher in the Dacca soil than in the Faridpur soil, whereas the order was just the reverse for bacterial numbers.

Greater formation of ammonia in the Dacca soil indicated that fungi are more active than bacteria in the decomposition of water hyacinth in soil, as the rise in ammonia content went hand in hand with the rise in fungal numbers in this soil.

Azotobacter numbers were smaller in the treated than in the control soils, presumably because of the competition of fungi and bacteria.

There was no sign of nitrogen fixation in a culture solution containing non-nitrogenous nutrients and water hyacinth as the source of energy and an inoculum of soil high in azotobacter. Water hyacinth, therefore, does not appear to be a satisfactory source of energy for nitrogen-fixing bacteria.

The soil experiments indicated that water hyacinth, if allowed to decompose in the soil, offers definite promise as a nitrogen-carrying manure.

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# INFLUENCE OF HEATING ON THE pH OF SOIL SUSPENSIONS

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In the course of some work on soil lime requirement, certain rapid methods were compared with the more direct one of adding lime in the laboratory and finding the amount required to bring the pH to approximate neutrality. At least 8 hours' shaking is required to bring a suspension of soil and lime water to equilibrium pH. This is inconvenient unless ample shaking equipment is available. An alternative method used in the Hawaiian sugar industry<sup>2</sup> is equally inconvenient. It appeared that a quick method, even if approximate, would be useful. The usual way of accelerating a chemical reaction is to apply heat, but no one seems to have used this method in the type of work mentioned.

## INFLUENCE OF HEATING ON LIMED SOIL SUSPENSIONS

In preliminary tests, the mixture of soil and lime water was simply heated to boiling for a few minutes and cooled. The final pH was found to be lower than that produced by long shaking, but results were not reproducible. In subsequent tests the mixtures were heated for various lengths of time in a boiling water bath and then cooled in running water.

A typical result (soil sample 3) is shown in figure 1. The amount of lime was estimated by the method of Featherstone<sup>3</sup> to be sufficient to produce approximate neutrality, and by the shaking method gave a pH of 6.7. It will be noticed that heating causes a rapid fall in pH for the first 5 or 10 minutes, after which a slow change occurs which is in all cases virtually complete after 30 minutes. The final pH is much below that found after shaking. The original pH of the unlimed soil was 5.4.

Measurements of pH were made by the glass electrode. Ten grams of soil was used together with 25 ml. of water or with a mixture of water and lime water. Heating was carried out in a 100-ml. long-necked flask.

## INFLUENCE OF HEATING ON UNLIMED SOIL SUSPENSIONS

It might appear that equilibrium between soil and lime is attained in 5 minutes and that the further drop in pH is due to other factors. This is not the case, as an unlimed soil suspension also shows a decrease in pH on heating for 5 minutes. Also if a soil suspension which has been heated with lime water is shaken for 8 hours, there is a further drop in pH. When equilibrium is so reached, the pH is lower than the "true" equilibrium value (defined as that produced by

<sup>1</sup> The writer thanks the Directors of the Irish Sugar Co., Ltd. for permission to publish this paper.

<sup>2</sup> Hance, F. E. Soil and plant analyses by rapid chemical methods: II. Hawaii. Sugar Planters' Assoc. Agr. and Chem. Ser. Bul. 51. 1937.

<sup>3</sup> Featherstone, J. Relationship between pH, lime requirement, and loss on ignition in soils. *Jour. Soc. Chem. Indus.* 57: 12. 1938.

shaking alone) by about the same amount as the pH of the unlimed soil suspension is lowered by 5 minutes' heating.

#### EFFECT OF TIME OF STANDING ON pH OF HEATED SOIL SUSPENSIONS

It was noted that suspensions which had been heated 30 minutes so that the pH had reached an equilibrium value showed, *in some cases*, a rise in pH when allowed to stand several days with occasional shaking. This applied both to unlimed and limed soils. The sample (No. 3) already discussed had a pH of

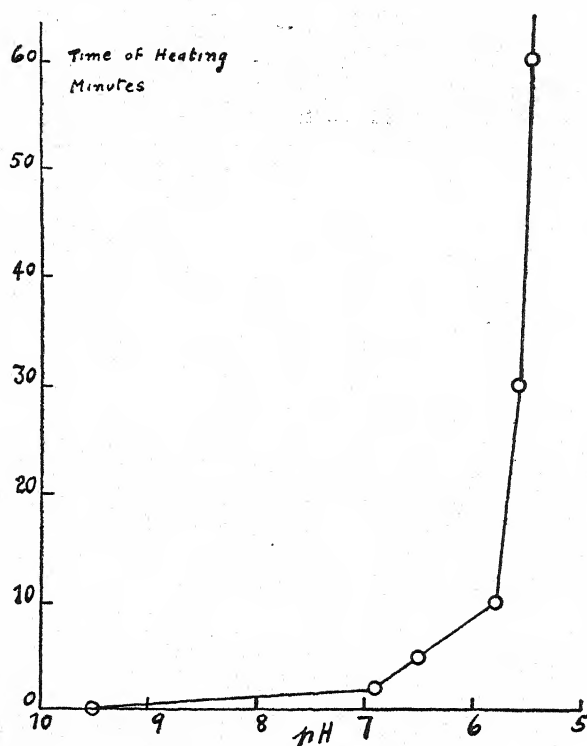


FIG. 1. CHANGE IN pH OF A SUSPENSION OF SOIL IN LIME WATER PRODUCED BY HEATING IN A BOILING WATER BATH

5.5 after 60 minutes' heating with lime. This value rose to 6.2 after several days. An unlimed soil suspension with an original pH of 5.6 had a pH of 5.1 after 30 minutes' heating. This value rose to 5.5 after several days.

#### EXPERIMENTAL RESULTS

Table 1 contains a selection from the many tests made. In all cases the amount of lime water added was that required to produce approximate neutrality and was estimated by the method already quoted. As the amount of shaking required to produce equilibrium depends on the type of soil, the following procedure was adopted for all samples except No. 8. The total time of



mechanical shaking was at least 10 hours (samples 1 and 7) but usually 16 to 18 hours, being continued until no further drop in pH occurred. As shaking was

TABLE 1

*Effect of heating in a boiling water bath on the pH of soil suspensions in water and lime water*

SAMPLE NUMBER	pH VALUES					
	Unlimed			Limed		
	Unheated	Heated 5 minutes	Heated 30 minutes	Heated 5 minutes	Heated 30 minutes	After shaking
1	5.2	4.7	4.4	6.7	5.6	6.5
2	6.2	6.0	6.0	6.4	6.2	6.7
3	5.6	5.0	4.8	6.7	6.1	6.7
4	5.9	..	5.2	6.9	6.0	7.0
5	5.3	..	4.7	6.1	5.6	6.4
6	6.8	6.4	6.6	..	..	..
7	5.6	5.0	4.8	6.5	5.5	6.7
8	4.9	4.8	4.8	8.1	7.3	7.5
9	5.2	4.8	4.6	6.2	5.5	6.3
10	4.8	4.8	4.6	6.6	5.8	6.6
11	5.0	..	4.4	6.3	5.7	6.3

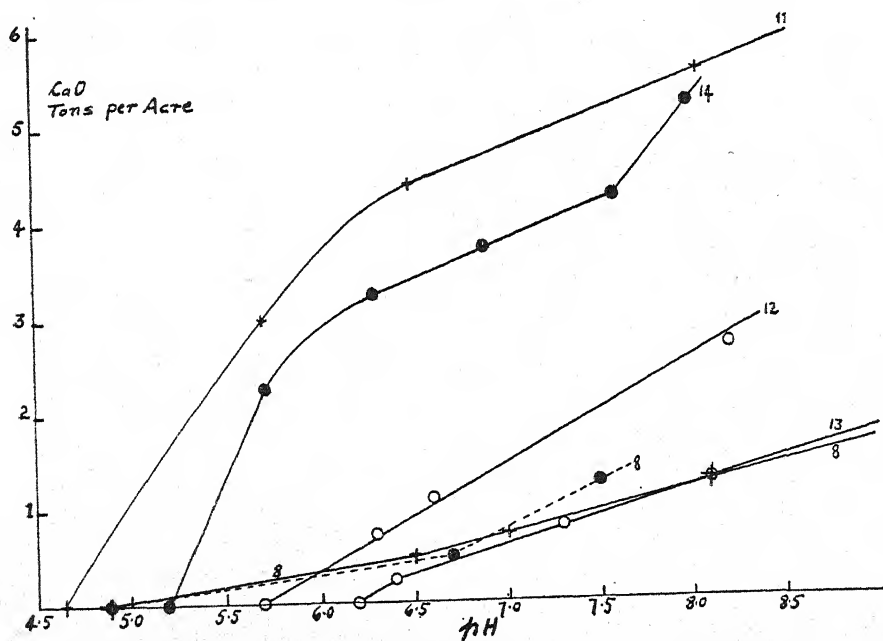


FIG. 2. SOIL BUFFER CURVES SHOWING CHANGES IN pH OF SOIL SUSPENSIONS TREATED WITH VARIOUS AMOUNTS OF LIME WATER AND HEATED FOR 5 MINUTES IN A BOILING WATER BATH

practicable only during the day, it was spread over at least 2 days in every case so that all samples also had one to three periods of standing overnight.

Results were also checked by allowing duplicate tests to stand for 3 to 8 days with occasional shaking for a few seconds two or three times a day. This was the only method used for sample 8, the pH of which after liming and standing with occasional shaking was 7.6 after 2 days and 7.5 after 4 and 5 days. In the other cases, results agreed within 0.1 or 0.2 pH with those given by mechanized shaking, except for sample 9, the pH of which was 6.2 after 2 days' standing with occasional shaking and 5.8 after 5 days. The figure 6.3 in table 1 was found after 24 hours' mechanical shaking spread over 3 days, the sample being allowed to stand overnight three times during the course of the test. From the result of this and other tests it seems possible that bacterial action may reduce the pH if the test is unduly prolonged.

As the pH ceases to fall, or falls only slightly, after 30 minutes' heating, a fairly accurate estimate of the true equilibrium value may be made as follows: Add a correction to the pH of the limed suspension after 30 minutes' heating. The correction is the difference between the original pH of the unlimed soil suspension and that obtained by heating the unlimed suspension for 30 minutes.

An alternative and much simpler procedure is recommended, however, particularly as it appears to give, on the average, a still better approximation to the required results. It is simply to accept the 5-minute value without any correction. The reaction with lime is incomplete in this period, which tends to make the result too high. The lowering effect of the heating approximately compensates for this.

For sample 8 where the 5 minutes' heating method gave the value 8.1 as against 7.5 by shaking, the soil was exceptionally sandy. It required only about 500 pounds CaO per acre to bring the pH from 7.5 to 8.1 and about 1 ton to bring it from 4.9 to neutrality (fig. 2).

Figure 2 shows some "buffer curves" prepared by heating soil suspensions with varying amounts of lime for 5 minutes and taking the uncorrected pH as being approximately the true equilibrium figure. For sample 8 the dotted line shows the results obtained by the shaking method. Lime addition is expressed as tons CaO per acre of topsoil, assumed to weigh 2,000,000 pounds. Graphs can be quickly determined without use of elaborate shaking devices.

#### SUMMARY

When a soil suspension in water is heated, its pH drops. When a suspension in lime water is similarly treated, the equilibrium pH is lower than the true equilibrium if the true equilibrium is defined as that produced by long shaking. The difference between the two equilibrium values is approximately the same as the drop in pH produced by heating the unlimed suspensions for the same time. These facts have been applied in devising a quick method for preparing soil buffer curves.

# INFLUENCE OF EARTHWORMS ON SOIL PRODUCTIVITY

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Ever since Darwin published his famous book, "The Formation of Vegetable Mould through the Action of Worms" (1), many persons have assumed that earthworms increase soil productivity. It is common knowledge that usually the number of earthworms parallels roughly the productivity of soils. Yet no one can deny that under certain conditions good crop growth can be obtained when earthworms are absent. Nutrient sand culture is an obvious example. Such exceptions have caused soil scientists to doubt the popular conception of the role earthworms play in soil productivity. The question is raised whether earthworms increase soil productivity or merely live in greater abundance in the better soils without really contributing to their productivity.

During the last half century, numerous attempts have been made to solve this problem (2). These researches, however, have been severely criticized by soil scientists. The basic criticism stems from the difficulty of testing earthworm activity while holding unchanged all other factors that influence plant growth. Whatever the virtues and shortcomings of these investigations, the fact remains that as yet no definitive evidence has been obtained to indicate that earthworm activity *per se* will increase the productivity of soil. As a result, most agricultural scientists have been indifferent to the possibility of using earthworms in farming.

The following report describes an experiment in which evidence was obtained that, under the specific conditions described, earthworms can markedly influence the productivity of soil. Because of the novel result, the experimental procedure is described in considerable detail.

## PROCEDURE

Twenty wooden barrels, measuring 32½ inches in height and 20 inches inside top diameter, were placed outdoors on cinder blocks, 8 inches above the ground. Five 1-inch holes were bored in the bottom of each barrel for water drainage. The inner walls were coated with black asphaltum to make them more nearly waterproof. The barrels were filled to within ½ inch of the top with an extremely impoverished clay subsoil.

The soil came from an airport on the National Research Center, Beltsville, Maryland. The topsoil, Tuxedo sandy loam, had been completely removed in the course of leveling the airport grounds, and the subsoil that remained supported only a sparse growth of weedy vegetation. It was devoid of earthworms, which is the reason it was selected for the experiment. Texturally, it consisted

<sup>1</sup> Erosion Control Practices Division, Soil Conservation Service, Research, U. S. Department of Agriculture, Beltsville, Maryland.

of 70 per cent clay, 12 per cent silt, 16 per cent sand, and 2 per cent gravel. It contained virtually no organic matter. Although the subsoil showed no zonal development, it was placed in the barrels with the top 6 inches of its profile on the surface. The underlying material was placed in the barrels without regard to its original position in the profile.

The barrels were filled between September 20 and 30, 1946. Fresh cow manure was worked into the top 3 inches at the rate of 130 gm. per barrel (2.9 tons per acre), oven-dry weight. An additional 120 gm. per barrel (2.7 tons per acre), oven-dry weight, was applied as a topdressing later the same fall. The soil was therefore heavily manured at the start. The pH of the soil was originally 5.2. It was brought to approximate neutrality by addition of hydrated lime at the rate of 68 gm. per barrel (1.5 tons per acre). In early October, each barrel was seeded with 42 grains of barley (60 pounds per acre) and 0.113 gm. bluegrass (5 pounds per acre), and 11.3 gm. of 5-10-5 fertilizer (500 pounds per acre) was added. In the spring of 1947, Korean lespedeza was seeded at the rate of 0.567 gm. per barrel (25 pounds per acre).

The 20 barrels were then paired, the two barrels of each pair being side by side. One of each pair was inoculated with living earthworms, and an equal number of killed earthworms was added to the other in order that all barrels should be equal in the amount of nutrients added by the bodies of the earthworms. The earthworms were killed by placing them in a test tube and immersing the tube for a moment in hot water.

During the short period of growing weather remaining that fall, development of the grain and grass was poor. The sparse vegetation gave little protection to the surface of the soil (3), and the earthworms died soon after they were placed in the barrels.

Nothing further was done with the barrels until September 1947, when the vegetation was cut off to the surface of the soil and weighed. By then the barrels bore a moderate stand of grass, weeds, lespedeza, and a small amount of clover. The clover was volunteer, having been introduced probably in the manure. There were no obvious differences among the barrels at that time.

On November 10, 1947, the ten pairs were treated according to the following plan:

- A. Pairs 1 and 2. All harvested vegetation replaced on the surface of the soil.
- B. Pairs 3 and 4. Same as treatment A plus 4-8-12 topdressing applied at the rate of 6.80 gm. per barrel (300 pounds per acre).
- C. Pairs 5 and 6. All harvested vegetation removed, and the surface of the soil covered with a single thickness of asphalt roofing paper.
- D. Pairs 7 and 8. Same as treatment C plus fertilizer applied as in treatment B.
- E. Pair 9. All harvested vegetation removed.
- F. Pair 10. Same as treatment E plus fertilizer applied as in treatment B.

The treatments were assigned in random arrangement among the ten pairs of barrels. The two pairs of treatment A, B, C, and D were duplicates, whereas treatments E and F were applied to single pairs.

On November 14, 1947, the barrels were reinoculated with earthworms that



had been gathered from several fields in the vicinity. The following earthworms were placed in each barrel: two mature *Lumbricus terrestris* L.; three mature *Helodrilus caliginosus* forma *trapezoides* Duges; two mature *Diplocardia* sp. Garman; one mature *Helodrilus chloroticus* Savigny; nine immature earthworms from a mixture of the three last species.

The total of 17 earthworms per barrel was equivalent to 339,000 per acre, a representative population for sodland in this vicinity (4). An equal number of killed earthworms was placed in the barrel of each pair that was not inoculated with living earthworms. The alimentary tract of the earthworms was evacuated of its previous content by storing the earthworms for one week in soil of the same kind as that used in the experiment.

During the winter of 1947-48, the barrels were exposed to the natural weather conditions. The soil froze and thawed rapidly where the surface was unprotected (treatments *E* and *F*) or protected only by the asphalt paper (treatments *C* and *D*). Freezing and thawing was much slower under the protection of the sod (treatments *A* and *B*), a condition conducive to winter survival of earthworms, as explained in previously reported findings (3, 4).

On March 8, 1948, the asphalt paper was removed from the barrels of treatments *C* and *D*. Warm weather followed, and the vegetation began to grow. On March 22, the barrels that had been topdressed the previous fall (treatments *B*, *D*, and *F*) were again topdressed with the same amount and kind of fertilizer. On April 15, the barrels that had received living earthworms were again reinoculated. The mixture used this time was somewhat different from that used in the fall, consisting of four each of *H. caliginosus* forma *trapezoides* and *H. chloroticus*. An equal number of killed earthworms was added to the barrels that did not receive living earthworms.

On June 18, 1948, the vegetation was harvested, assorted by kinds, air-dried, and weighed. Thereafter, infiltration tests were made on the soil in the barrels. These were conducted by driving a steel cylinder, 4½ inches in diameter, into the soil to a depth of approximately 3 inches. The soil within the cylinder was wetted and then the rate of infiltration was determined by measuring the water required to keep a constant head over the soil surface. A graduated Mariotte bottle was used to maintain the head.

#### RESULTS

Differences in vegetation between barrels that had been inoculated with living earthworms and those that had not were little short of extraordinary (fig. 1). Where the clippings had been replaced so that the soil had been protected over winter (treatments *A* and *B*), the inoculated barrels bore a luxuriant growth of vegetation. The highest yield, 103.7 gm. was equivalent to 2.28 tons air-dry weight per acre (table 1). This yield was far above expectations for a soil of such low natural productivity. Barrels treated similarly, but not inoculated, bore only a moderate growth of vegetation. Where the protective cover over winter had been inadequate (treatments *C*, *D*, *E*, and *F*), however, addition of living earthworms had little effect on the vegetation in two out of three cases.



For ease of comparison, the yield totals in table 1 were transformed to tons per acre, and the results are shown in table 2. Where the soil was protected with clippings, inoculation with earthworms apparently increased yields by 1.12 tons per acre without the topdressing, and by 1.36 tons with the topdressing. Where the clippings were removed and asphalt paper was placed on the surface instead, the apparent effect of the inoculation was far less: an increase of 0.30 ton without topdressing and 0.43 ton with topdressing.



FIG. 1. GROWTH OF VEGETATION ON JUNE 16, 1948, IN A PAIR OF BARRELS, ONE (RIGHT) INOCULATED WITH LIVING EARTHWORMS, THE OTHER, UNINOCULATED

The inoculated barrel bore approximately four times the weight of vegetation on an air-dry basis. Both barrels had been given equal amounts of manure, lime, and fertilizer. The background lines are 1 foot apart.

Where the clippings had been removed and no artificial protection given, a condition unfavorable for winter survival of earthworms, the apparent effect of the inoculation was 1.06 tons without topdressing and  $-0.58$  ton with topdressing. These results, however, are somewhat deceptive because another factor besides the earthworms entered into the observed effects. During the spring of 1948, a colony of small ants<sup>2</sup> infested the barrel that had received fertilizer but no living worms. The ants formed a trail up the outside of the barrel

<sup>2</sup> Identified as the pavement ant (*Tetramorium caespitum* L.) by M. R. Smith, Bureau of Entomology and Plant Quarantine.

and burrowed into the soil. During several weeks of activity in May and June, they deposited a large quantity of finely pulverized soil on the surface. At least half the surface was covered with this fine material up to 1 inch in depth.

TABLE 1  
*Vegetation harvested on June 18, 1948 from barrels variously treated*  
Grams per barrel, air-dry basis

TREATMENT	PAIR	INOCULATED WITH LIVING WORMS					NOT INOCULATED WITH LIVING WORMS				
		Grass	Clover	Lespe- deza	Weeds	Total	Grass	Clover	Lespe- deza	Weeds	Total
A	1	26.9	28.6	8.8	0.0	64.3	11.6	0.8	0.3	0.4	13.1
	2	12.2	54.8	0.0	0.0	67.0	6.1	3.1	6.9	0.0	16.1
B	3	36.9	66.8	0.0	0.0	103.7	23.8	0.0	4.0	0.0	27.8
	4	15.3	52.4	0.0	7.0	74.7	16.4	9.8	0.6	0.1	26.9
C	5	11.4	7.1	6.3	0.2	25.0	7.5	0.0	5.6	2.5	15.6
	6	12.7	5.4	2.6	5.5	26.2	4.5	0.1	2.6	0.4	7.6
D	7	12.5	0.0	0.1	8.9	21.5	5.7	12.9	0.0	4.6	23.2
	8	60.4	0.0	0.0	0.4	60.8	9.8	5.2	0.0	4.0	19.0
E	9	2.9	55.4	0.0	0.0	58.3	9.3	0.0	0.0	0.5	9.8
F	10	28.4	0.0	0.0	0.4	28.8	16.4	37.6	0.0	1.0	55.0*

\* Infested with ants; see discussion in text.

TABLE 2  
*Effect of earthworm inoculation on yields from barrels variously treated*  
Tons per acre, air-dry basis

OVER-WINTER TREATMENT	TOPDRESSED IN FALL AND SPRING	YIELD OF VEGETATION		
		Inoculated with Living Worms	Not Inoculated with Living Worms	Apparent Effect of Inoculation
Clippings on surface	No	1.41, 1.47	0.29, 0.35	1.12
	Yes	1.64, 2.28	0.59, 0.61	1.36
Clippings removed; asphalt paper on surface	No	0.55, 0.58	0.17, 0.34	0.30
	Yes	0.48, 1.34	0.43, 0.51	0.43
Clippings removed	No	1.28	0.22	1.06
	Yes	0.64	1.22*	-0.58

\* Infested with ants; see discussion in text.

This activity of the ants stimulated development of clover, and by the time the vegetation was harvested, the growth in this barrel had become noticeably superior to that in the other barrel of the pair. There was no evident reason

why ants infested only this one barrel; apparently it had nothing to do with the treatment. As shown in table 2, of the ten barrels that had not been inoculated with living earthworms, the ant-infested barrel was the only one that developed a luxuriant growth of vegetation. The burrowing activity of the ants was evidently very beneficial in this clay soil.

TABLE 3  
*Proportion of clover in harvested vegetation*  
Air-dry basis

OVER-WINTER TREATMENT	TOPDRESSED IN FALL AND SPRING	CLOVER IN VEGETATION	
		Inoculated with Living Worms	Not Inoculated with Living Worms
		<i>per cent</i>	<i>per cent</i>
Clippings on surface	No	44, 82	6, 19
	Yes	64, 70	0, 36
Clippings removed; asphalt paper on surface	No	21, 28	0, 1
	Yes	0, 0	27, 56
Clippings removed	No	95	0
	Yes	0	68*

\* Infested with ants; see discussion in text.

TABLE 4  
*Infiltration rates of soil in barrels variously treated*  
Inches per minute

OVER-WINTER TREATMENT	TOPDRESSED IN FALL AND SPRING	INFILTRATION RATE OF SOIL		
		Inoculated with Living Worms	Not Inoculated with Living Worms	Apparent Effect of Inoculation
Clippings on surface	No	1.32, 1.53	0.28, 0.32	1.12
	Yes	0.58, 1.04	0.24, 0.26	0.56
Clippings removed; asphalt paper on surface	No	0.11, 0.15	0.06, 0.29	-0.04
	Yes	0.00, 0.19	0.06, 0.20	-0.03
Clippings removed	No	0.10	0.02	0.08
	Yes	0.17	0.45*	-0.28

\* Infested with ants; see discussion in text.

The data in table 1 give the harvested yields of vegetation by species. There was an outstanding difference among the barrels in this respect also. In the barrels with high yields, the vegetation consisted largely of clover; whereas in the barrels with low yields, it was largely grasses, weeds, and lespedeza. In table 3, the proportion of clover in the vegetation is listed by treatments. Stimulation of the clover occurred as well in the barrel infested by ants as in those inoculated with living earthworms.

The increased yields apparently attributable to the earthworms were associated with noticeable improvement in infiltration rate of the soil (table 4). Where living earthworms had been introduced and the soil surface protected over winter with clippings, water entered the soil three to four times more rapidly than where living earthworms had not been introduced or where they had been introduced but unsuitable cover conditions had been maintained for their survival. The infiltration rate for the barrel that became infested with ants was of special interest. It was greater than for any of the other uninoculated barrels. These data indicate that the effect of the earthworms and ants on soil structure was of major importance.

#### DISCUSSION

It is well to refer back to the question raised at the start of this paper: Do earthworms increase soil productivity or merely live in greater abundance in the better soils without contributing to productivity? The soil used in this experiment was unproductive by all standards of fertility. Where living earthworms were not introduced, the vegetation was relatively poor, both with and without cover conditions normally favorable for the over-winter development of earthworms. Furthermore, the unfavorable conditions were not eliminated by addition of manure, lime, or fertilizer or by cultivation of the soil in the original preparation of the seedbed. Where living earthworms were introduced and favorable cover conditions were maintained, the vegetation grew luxuriantly.

Since the apparent benefit of the earthworms was more pronounced where suitable over-winter cover was maintained, it would seem that the earthworms introduced in the fall of 1947 were more important than those introduced the following spring.

It was interesting to find that ants produced the same benefits as the earthworms. Though widely different in life habits, both animals loosen the soil. It may be surmised, therefore, that improved soil structure accounted for the stimulating effect of the earthworms on the vegetation. These results suggest, further, that the soil structure resulting from the action of diverse fauna may well be a factor of significance to soil productivity.

Despite the remarkable effect apparently attributable to the earthworms, a word of warning is in order against generalizing too broadly from this experiment. The soil was fine-textured and had poor structure. It presented a specific complex of limiting factors that were corrected by earthworm activity. Some soil is so coarse-textured that structure seldom limits crop growth. On soils where crop growth is limited by factors other than those amendable by earthworm activity, increased yields as obtained in this experiment cannot be anticipated.

Though few soils used for agriculture are as poor as the one in this experiment, the results do have an important bearing on the maintenance of productivity in farm soils. Much of our agricultural land consists of fine-textured soils and, on these, decline in structure is widely recognized as an important problem. Here earthworms can be expected to have beneficial effects like those observed in this experiment.

Finally, the authors want to emphasize that the earthworms were placed in the barrels solely for experimental control. The procedure is not intended to suggest any need for artificially planting earthworms in fields. Earthworms are already widely distributed. Often they are killed by bad land management, but, as recently reported (3), they can be restored by proper cultural methods.

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# DETERMINATION OF CATION- AND ANION-EXCHANGE PROPERTIES OF SOILS<sup>1</sup>

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Information on the exchange properties of soils is essential to an understanding of many problems in the fields of soil chemistry and plant nutrition. The properties most frequently measured are the cation-exchange capacity and the exchangeable cations. A characterization of the chemical properties of soils frequently requires determination of the rate of release of cations, the anion-exchange capacity, and the degree of anion saturation. There is need for development and improvement of methods for measuring these properties. This paper is concerned with a description of methods for measuring the cation-exchange capacity, exchangeable H, Ca, Mg, K, and Na, the anion-exchange capacity, and  $\text{NH}_4\text{F}$ -replaceable P.

The methods for cation-exchange properties are modifications of the  $\text{BaCl}_2$ -triethanolamine procedures (15) previously proposed for the "rapid, approximate determination of base-exchange capacity and exchangeable hydrogen" (16). Although quantitative procedures have been adopted, the rapid aspects of the method have been retained to some extent by use of semimicrocolorimetric techniques and use of the centrifuge. For the determination of Mg, thiazol yellow has been substituted for titan yellow. Calcium is determined volumetrically in the presence of Ba using  $\text{KMnO}_4$ . Potassium and Na are determined colorimetrically or with the flame photometer. The indirect determination of Ba for cation-exchange capacity is modified in that the Ba is replaced with  $\text{CaCl}_2$  and the Ba determined colorimetrically as  $\text{BaCrO}_4$ . The Ca-soil is then used to determine the equilibrium pH with  $\text{H}_3\text{PO}_4$  and the anion-exchange capacity. These values, together with the cation-exchange capacity, are taken as a measure for characterizing soil colloid properties. The exchangeable  $\text{PO}_4$  is determined by replacement with acidified  $\text{NH}_4\text{F}$ . For the colorimetric measurement of P the vanadate-molybdic acid method has been adopted. Detailed descriptions of the procedures are given, together with some results and a discussion of factors influencing the results.

## THE METHOD

### *Replacement of cations*

*Replacement solution A.* Barium chloride-triethanolamine: Dilute 90 ml. of commercial triethanolamine (sp. gr. 1.126) with 1000 ml. of  $\text{H}_2\text{O}$  and partly neutralize with HCl to adjust to pH 8.1. This requires about 280 to 300 ml. of

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*N HCl.* Make up to 2 liters with  $H_2O$  and mix with 2 liters of a solution containing 100 gm. of  $BaCl_2 \cdot 2H_2O$ . Protect from  $CO_2$  of the air during storage.

*Replacement solution B.* Barium chloride: Dissolve 25 gm.  $BaCl_2 \cdot 2H_2O$  in 1 liter of  $H_2O$ .

*Procedure:* Weigh an amount of soil sufficient to give 0.5 to 2.5 m.e. cation-exchange capacity (air-dried and screened through a 1-mm. sieve) into a crucible holder mounted on a 250-ml. volumetric phosphorus flask having a wide neck and containing a moistened filter paper disc.<sup>2</sup> Place a small layer of absorbent cotton on top of the soil. Leach with 100 ml. of solution A contained in a volumetric flask. The flask should be suspended above the soil so as to require at least 4 hours for the passage of 100 ml. of solution A. After this solution has thoroughly drained, add 25 ml. of solution B with graduated cylinder. Rinse the sides with about 20 ml. of  $H_2O$  and finally wash with 100 ml.  $H_2O$  using suction if desired. Make the combined leachates and washings up to a volume of 250 ml. and mix thoroughly. Aliquot portions of this extract are then used for measuring the exchangeable H, Ca, Mg, K, and Na. (For further treatment of the residue see "Cation-exchange capacity.")

#### *Exchangeable hydrogen*

*Reagents:* 1. Hydrochloric acid, 0.04 *N*.

2. Mixed indicator. Triturate 0.1 gm. of brom cresol green indicator with 14.3 ml. of 0.01 *N* NaOH and dilute to 200 ml. with  $H_2O$ . Dissolve 0.1 gm. of methyl red in 200 ml. of 95 per cent ethanol. Mix the indicators to consist of 2 parts of brom cresol green and 3 parts of methyl red.

*Procedure:* Measure 50 ml. of the soil leachate into a flask or beaker, add 6 drops of mixed indicator, and titrate with HCl to pink. The hydrogen, in milliequivalents, in the soil is the difference between the titration of the unknown and the titration of a 20-ml. aliquot of replacement solution A.

#### *Exchangeable calcium*

*Reagents:* 1. Sulfuric acid, approximately 0.2 *N*.

2. Ammonium oxalate-ammonium acetate mixture. Dissolve 25 gm.  $(NH_4)_2C_2O_4 \cdot H_2O$  and 50 gm.  $NH_4C_2H_3O_2$  in 1 liter of  $H_2O$ .

3. Saturated solution of calcium oxalate.

4. Potassium permanganate and Ca standard: Dissolve 0.65 gm.  $KMnO_4$  in 1 liter of  $H_2O$ . After 48 hours, siphon into a brown bottle leaving undisturbed at the bottom any residue formed. Standardize against known amounts of Ca by the regular procedure. Dissolve 1.0008 gm. of  $CaCO_3$  (Iceland spar for standardization) in about 200 ml. of  $H_2O$  to which is added 25 ml. of *N* HCl and make to 1 liter with  $H_2O$ . Add 0 to 20 ml. of the Ca solution to 50-ml. portions of replacement solution (95 ml. of A, 25 ml. of B, and 130 ml. of  $H_2O$ ) and proceed as directed below. (Before proceeding, see "Magnesium standard.")

*Procedure:* Measure 50 ml. of the soil leachate into a 150- or 200-ml. beaker

<sup>2</sup> Special crucible holders with porcelain disc permanently mounted and with provision for suction are obtainable from Southern Scientific Co., Inc., Atlanta 3, Georgia.

and heat just to boiling. Add 25 ml. of 0.2 *N* H<sub>2</sub>SO<sub>4</sub>, stir, and then add slowly with stirring 10 ml. of the oxalate-acetate mixture. Allow to digest for about 2 hours, and filter with suction through Gooch crucibles or porcelain filtering crucibles with porous bottoms. Rinse the beaker, and wash the precipitate four times with saturated solution of calcium oxalate. Put the crucible containing the precipitate into the original beaker, add enough hot 0.2 *N* H<sub>2</sub>SO<sub>4</sub> to cover the crucible, stir thoroughly, and titrate with KMnO<sub>4</sub>. (Ml. of KMnO<sub>4</sub> × normality × 5 ×  $\frac{100}{\text{gm. soil used}}$  = m.e. Ca per 100 gm.)

#### *Exchangeable magnesium*

*Reagents:* 1. Sodium hydroxide. Dissolve 30 gm. of NaOH, low in carbonate, in 100 ml. of H<sub>2</sub>O.

2. Thiazol yellow. Dissolve 0.1 gm. of thiazol yellow in 500 ml. of H<sub>2</sub>O. Store in a cool place and make up fresh every 2 months.

3. Magnesium standard and calibration curve. Dissolve 1.2325 gm. of MgSO<sub>4</sub>·7H<sub>2</sub>O in 1 liter of H<sub>2</sub>O to give 0.01 *N* Mg. Add 0, 0.5, 1.0, 2.0, 4.0, and 8 ml. of the Mg standard to 150- or 200-ml. beakers containing 50 ml. of the replacement solution. This is conveniently done in the same solutions used for the standardization of KMnO<sub>4</sub> (see "Exchangeable calcium"). Proceed as directed under exchangeable Ca and under Mg below. From the resultant data, construct a calibration curve for the 0-, 0.5-, 1.0-, and 2.0-ml. increments of Mg and another for the 2.0-, 4.0-, and 8.0-ml. increments of Mg in a 1:3 dilution, by plotting the transmission against milliequivalents Mg.

*Procedure:* Make up the filtrate from the Ca precipitation to a volume of 100 ml. Pipette 20 ml. of the clear filtrate into a vial or flask, add 1 ml. of thiazol yellow, mix, add 2 ml. of NaOH, mix, and within 2 minutes measure the transmission of the solution at 525 mμ. Use a water blank for the 0 setting of the instrument. If the concentration of Mg is too high, use a 5-ml. aliquot diluted with 15 ml. of H<sub>2</sub>O.

#### *Exchangeable potassium*

*Reagents:* 1. Sodium carbonate. Dissolve 26 gm. of c.p. Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O in 95 ml. of H<sub>2</sub>O.

2. Sodium cobaltinitrite. Dissolve 40 gm. of K-free Co(NO<sub>2</sub>)<sub>3</sub>·2NaNO<sub>2</sub> in 100 ml. of H<sub>2</sub>O and filter. Prepare this solution as needed.

3. Sodium acetate, nitroso-R-salt solution. Dissolve 0.5 gm. of nitroso-R-salt in 750 ml. of H<sub>2</sub>O, then add 100 gm. of NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O, dissolve, and make up to 1 liter.

4. Acetic acid, 10 per cent by volume.

5. Nitric acid wash solution, approximately 0.01 *N*.

6. Potassium standard and calibration curve. Prepare 0.01 *N* KCl by dissolving 0.7456 gm. of dried KCl in 1000 ml. of H<sub>2</sub>O. Add increments of 0 to 3.0 ml. of this solution to 250-ml. volumetric flasks containing 95 ml. of replacement solution A and 25 ml. of solution B. Make up to volume with H<sub>2</sub>O and mix.

Determine K according to the procedure below. From the resulting data construct a calibration curve by plotting the transmission against milliequivalents K.

*Procedure:* To 60 ml. of the soil leachate add 2 ml. of sodium carbonate, mix thoroughly, and filter after about 20 minutes into a 50-ml. beaker. Measure out 50 ml. and return to the same beaker after discarding the excess. Evaporate to dryness, avoiding temperatures higher than 70° as evaporation approaches completion. Rinse the sides with 5 ml. of acetic acid, dissolve, and transfer the entire content into a 15-ml. centrifuge tube. Add 3 ml. of sodium cobaltinitrite, mix thoroughly, and place in a refrigerator at about 10° C. for 6 hours or for overnight. Centrifuge for 15 minutes at 2000 r.p.m., decant, drain by placing the tube at a 45° angle, rinse the mouth of the tube with cool wash solution, and then add 5 ml. to the tube. Break up the precipitate, and centrifuge for 10 minutes. After draining, add 10 ml. of H<sub>2</sub>O and then rapidly 1 ml. of concentrated H<sub>2</sub>SO<sub>4</sub>, shake or stir until dissolved. Measure 2 ml. into a vial or small flask and add 20 ml. of the sodium acetate-nitroso-R-salt solution and mix. After 30 minutes measure the transmission of the solution at 525 mμ. As a blank for the zero setting, use the solution of the sodium acetate-nitroso-R-salt but containing 0.5 ml. of concentrated H<sub>2</sub>SO<sub>4</sub> per 100 ml. This solution can also be used for dilution of the unknown when the concentrations of K are too high for direct reading. Make this dilution after 30 minutes' standing.

#### *Exchangeable sodium*

*Reagents:* 1. Ammonium carbonate. Dissolve 25 gm. of c.p. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> cubes (Na-free) in 100 ml. of H<sub>2</sub>O.

2. Uranyl magnesium acetate. Dissolve 32 gm. of UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O and 100 gm. of Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O in H<sub>2</sub>O by warming. Cool, add 20 ml. of 99.5 per cent acetic acid and 475 ml. of 95 per cent ethanol; dilute with H<sub>2</sub>O to 1 liter and mix. Filter after 2 days and store in a Pyrex bottle in the dark. Prepare fresh after 4 weeks.

3. Ethyl acetate-acetic acid wash solution. Dilute 300 ml. of ethyl acetate to 1 liter with 99.5 per cent acetic acid.

4. Ethyl ether, c.p. anhydrous.

5. Sulfosalicylic acid. Dissolve 12.5 gm. of sulfosalicylic acid in H<sub>2</sub>O and dilute to 250 ml. Titrate a 5-ml. aliquot with 0.1 N NaOH using phenolphthalein as the indicator and adjust exactly to 0.35 N.

6. Sodium acetate, 10 per cent.

7. Sodium standard and calibration curve. Prepare 0.01 N NaCl by dissolving 0.5845 gm. of the salt in 1000 ml. of H<sub>2</sub>O. Add 0, 1.0, 2.5, 5.0, 10, and 25 ml. of the standard to 250-ml. volumetric flasks containing 95 ml. of replacement solution A and 25 ml. of solution B. Make up to volume with H<sub>2</sub>O and mix. Determine Na according to the procedure below. Construct a calibration curve from the 0-, 1-, 2.5-, 5-ml. increments and another from the 5-, 10-, and 25-ml. increments in an 1:4 dilution, by plotting the transmission against milliequivalents Na.

*Procedure:* To 60 ml. of the soil leachate add 2 ml. of ammonium carbonate,



mix thoroughly, and filter after 20 minutes into a 50-ml. beaker. Measure out 50 ml. and return it to the same beaker after discarding the excess. Evaporate to dryness, avoiding temperatures higher than 70° C. as evaporation approaches completion. Rinse the sides with small amounts of H<sub>2</sub>O and evaporate again. Add 2 ml. of 0.2 N HNO<sub>3</sub>, dissolve, and transfer the entire contents into a 15-ml. centrifuge tube; add 5 ml. of uranyl magnesium acetate and stir vigorously. Allow to stand in a water bath between 15 and 20° C. for 1½ hours. Centrifuge for 15 minutes at 2000 r.p.m., decant, and drain for several minutes. Wash the mouth with ethyl acetate-acetic acid wash solution, and then add 4 ml. of this solution down the sides of the tube. Break up the precipitate with a stirring rod, rinse the rod with about 0.5 ml. of the wash solution, and centrifuge for 10 minutes. Decant, drain, wash the mouth with ethyl ether, add 4 ml. of ethyl ether down the sides, break up the precipitate with a stirring rod, rinse with 1 ml., and centrifuge for 8 minutes. Decant, drain for not more than 1 minute, and dissolve the precipitate in 10 ml. of H<sub>2</sub>O. Introduce 5 ml. of the solution into a dry vial, add 1 ml. of 0.35 N sulfosalicylic acid, and mix. Then add 1 ml. of sodium acetate, mix, and after 15 minutes measure the transmission at 450 mμ. Use a water blank for the 0 setting.

*Exchangeable potassium and sodium-flame photometer procedure*

*Potassium and sodium standard:* Measure 0 to 5 ml. of 0.01 N KCl and NaCl into 250-ml. volumetric flasks containing 100 ml. of replacement solution A and 25 ml. of solution B. Make up to volume with H<sub>2</sub>O. Transfer 50-ml. portions into Erlenmeyer flasks and add 2 ml. of 25 per cent ammonium carbonate, mix, and filter after 20 minutes. Prepare calibration curves by plotting the flame photometer readings against milliequivalents K or Na.

*Procedure:* Remove the Ba from a 50-ml. aliquot of the soil extract with 2 ml. of ammonium carbonate, and measure the concentration of K or Na as above. If the concentration of K or Na exceeds that corresponding to 5 ml. of 0.01 N, dilute with the blank solution. (Procedure adapted to the Perkin Elmer Flame Photometer, Model 52-A.)

*Determination of aluminum*

*Reagents:* 1. Aluminon. Dissolve 0.2 gm. of aluminon (ammonium salt of aurin tricarboxylic acid) in 100 ml. of H<sub>2</sub>O. Store in an amber glass dropping bottle; prepare fresh every 6 months.

2. Starch solution. To 1 gm. of c.p. soluble starch add a few drops of water and make a paste. Add slowly, with stirring, 100 ml. of boiling distilled water and filter. Prepare daily as needed.

3. Hydroxylamine hydrochloride, 5 per cent in water.

4. Aluminum standard and calibration curve. Prepare 0.01 N Al by dissolving 0.4024 gm. AlCl<sub>3</sub>·6H<sub>2</sub>O in 500 ml. H<sub>2</sub>O. Add to 25-ml. volumetric flasks 0 to 1 ml. of the Al solution, 10 ml. of replacement solution A, 2.5 ml. of solution B, and make up to volume with H<sub>2</sub>O. Measure 2-ml. portions into vials and proceed as given below. Plot the transmission against milliequivalents Al.



*Procedure:* Measure 2 ml. of the soil extracts into a vial, add 2 ml. of 0.04 N HCl and 2 drops hydroxylamine hydrochloride, mix, add 1 ml. starch solution and 2 drops of aluminon solution. Mix thoroughly and, at the end of 30 minutes, read in an electrophotometer at 525  $m\mu$ . Use a water blank for 0 setting. If the Al concentration is too high, take 1 ml. of the extract and dilute with 1 ml. of the replacement solution (10 ml. replacement solution A, 2.5 ml. of solution B, and 12.5 ml. H<sub>2</sub>O).

#### *Cation-exchange capacity*

*Reagents:* 1. Calcium chloride. Dissolve 50 gm. c.p. CaCl<sub>2</sub>·2H<sub>2</sub>O in 1 liter of H<sub>2</sub>O and add a few milliliters of a saturated solution of Ca(OH)<sub>2</sub>, sufficient to adjust to approximately pH 8.

2. Potassium chromate, 10 per cent.

3. Saturated solution of barium chromate.

4. Dilute HCl, 1:4 by volume.

5. Barium standard and calibration curve. Measure 0.5 to 5 ml. of 0.05 N BaCl<sub>2</sub> (6.1078 gm. BaCl<sub>2</sub>·2H<sub>2</sub>O per liter of H<sub>2</sub>O) into 25-ml. volumetric flasks containing 12.5 ml. of CaCl<sub>2</sub>, make up to volume with H<sub>2</sub>O, and mix. Measure 10-ml. portions into 15-ml. centrifuge tubes, add 1 ml. of K<sub>2</sub>CrO<sub>4</sub>, mix, and proceed as directed below. Plot the instrument readings against the concentrations of Ba.

*Procedure:* Leach the Ba-saturated soil with 125 ml. of CaCl<sub>2</sub> and collect the leachate in a 250-ml. volumetric flask. Rinse the sides with about 20 ml. of H<sub>2</sub>O and then wash with 100 ml. of H<sub>2</sub>O. Make the leachate up to volume with H<sub>2</sub>O and mix. Pipette 10 ml. into a 15-ml. centrifuge tube, add 1 ml. of K<sub>2</sub>CrO<sub>4</sub>, and place in a water bath heated to 80–90° C. After 20 to 30 minutes, shake the tube to allow complete settling of the precipitate. When settling is complete, requiring about 2 hours, cool to room temperature, centrifuge for 15 minutes at 1700 r.p.m., decant, and allow to drain. Rinse the mouth of the tube and then wash down the sides with about 5 ml. of saturated BaCrO<sub>4</sub> solution. Break up the precipitate, rinse the stirring rod, again centrifuge, decant, and drain. Dissolve precipitate in 10 ml. of dilute HCl and mix thoroughly. Measure the transmission at 425  $m\mu$ , using a water blank for the 0 setting.

#### *Anion-exchange capacity and equilibrium pH (pH<sub>e</sub>)*

*Reagents:* 1. Phosphoric acid, 0.01 M H<sub>3</sub>PO<sub>4</sub> or 0.01 N in terms of the first H. Measure 0.4 ml. of 85 per cent H<sub>3</sub>PO<sub>4</sub> into a liter volumetric flask and make up to volume with H<sub>2</sub>O. Standardize against 0.04 N NaOH using the mixed indicator.

2. Sodium hydroxide 0.04 N. Dissolve 1.8 gm. NaOH in 1 liter of H<sub>2</sub>O and standardize against 0.04 N HCl (see "Exchangeable hydrogen").

3. Ammonium vanadate. Dissolve 1.25 gm. of NH<sub>4</sub>VO<sub>3</sub> in 300 ml. of 1:2 (by volume) HNO<sub>3</sub> and heat until solution is complete. Allow to cool, and make up to 500 ml. with 1:2 HNO<sub>3</sub>.

4. Ammonium molybdate. Dissolve 25 gm. of ammonium molybdate in 400 ml. of H<sub>2</sub>O, and make up to 500 ml. Do not heat over 50° C.

5. Phosphorus standard. Measure 0 to 1 ml. of 0.01  $M$   $H_3PO_4$  into vials, diluting in each case with  $H_2O$  to give a total volume of 10 ml. Add 1 ml. of ammonium vanadate, mix, then add 1 ml. of ammonium molybdate while mixing, and after 15 minutes measure the transmission at 430  $m\mu$ . Plot the instrument readings against  $PO_4$  adsorbed as follows: 1 ml. of P standard = 0; 0.8 ml. = 0.2; 0.6 ml. = 0.4, etc.

*Procedure:* Weigh enough of the Ca-soil to give 0.25 m.e. cation-exchange capacity into an Erlenmeyer flask, and add 25 ml. of 0.01  $N$   $H_3PO_4$ . Shake for 30 minutes, allow to sit for 24 hours, and again shake for 30 minutes. Determine the pH of the suspension with a glass electrode. Filter through a highly retentive paper, discarding the first few milliliters. Measure 1 ml. of the filtrate into a vial, add 9 ml. of  $H_2O$  and 1 ml. of  $NH_4VO_3$ , mix, then add 1 ml. of ammonium molybdate while stirring, and after 15 minutes read the transmission. As a blank use 10 ml. of  $H_2O$  and 1 ml. each of the vanadate and molybdate solutions respectively. The anion-exchange capacity in millimols per 100 gm. soil is obtained by multiplying the cation-exchange capacity by the  $PO_4$  adsorbed and by adding the millimols of exchangeable phosphorus.

#### *Exchangeable phosphorus*

*Reagents:* 1. Extracting solution. Dissolve 2.25 gm. of  $NH_4F$  in a liter of 0.05  $N$   $HCl$ . This gives a solution 0.06  $N$   $NH_4F$  at pH 3.0.

2. Phosphorus standard. Measure 0.2 to 1 ml. of 0.01  $M$   $H_3PO_4$  into vials and make up to 10 ml. with the extracting solution. Add 1 ml. of 0.25 per cent ammonium vanadate, mix, then add 1 ml. of 5 per cent ammonium molybdate while mixing, and after 15 minutes measure the transmission at 430  $m\mu$ . Plot the instrument readings against millimols of  $PO_4$  multiplied by 100.

*Procedure:* Weigh 2.5 gm. of the Ca-soil into an Erlenmeyer flask and add 25 ml. of the extracting solution. Shake for 30 minutes, transfer into a 50-ml. Lusteroid centrifuge tube, and centrifuge at 3000 r.p.m. for 15 minutes. Measure 10 ml. of the clear filtrate into a vial, add 1 ml. of ammonium vanadate, mix, then add 1 ml. of ammonium molybdate while mixing, and after 15 minutes read the transmission. As a blank use 10 ml. of the extracting solution and 1 ml. each of the vanadate and molybdate solutions, respectively. The millimols of exchangeable  $PO_4$  per 100 gm. soil are read directly from the standard curve. If the concentration of P in the extract is too high, take a proportionately smaller aliquot of the soil extract, dilute with extracting solution to a volume of 10 ml. and develop the color as before.

#### *Preliminary treatment of soils containing carbonates*

The characterization of soil from the standpoint of its equilibrium pH and the anion-exchange properties by the proposed procedure requires a soil free of carbonates. Test for effervescence by treating the original soil with  $HCl$ . The soil showing evidence of carbonates is treated as follows: Weigh 10-gm. portions of soil into 300-ml. Erlenmeyer flasks, add 200 ml. of 2 $N$   $NH_4Cl$ , and heat to boiling 1 to 2 hours or until no  $NH_4$  perceptibly volatilizes. Add more  $NH_4Cl$  if necessary. Filter through a Büchner funnel, wash with copious amounts of

H<sub>2</sub>O, leach with 100 ml. of BaCl<sub>2</sub>-triethanolamine, then with 50 ml. of 0.2 N BaCl<sub>2</sub>, and finally with 150 ml. of H<sub>2</sub>O. Dry, mix, weigh out a suitable amount of soil, replace the Ba with CaCl<sub>2</sub>, and determine the cation-exchange capacity as previously described. If the characterization is to be made for the mineral fraction of the soil only, the organic matter is oxidized with H<sub>2</sub>O<sub>2</sub> in the usual manner (23). The residue is then washed with copious amounts of H<sub>2</sub>O, saturated with Ba as above, and the cation-exchange capacity determined as before.

## RESULTS AND DISCUSSION

### *Exchangeable cations*

The preliminary separation of Ba from Ca is tedious and inaccurate. The concentration of Ba in the present procedure is not too high to permit determination of Ca in the presence of Ba. The method finally recommended is expeditious and yields reproducible results. It is important to standardize the KMnO<sub>4</sub> against known amounts of Ca carried through the regular procedure. The recovery of Ca under these conditions is only about 90 to 95 per cent of the theoretical; hence, details of the instructions must be followed explicitly. The method for determining the exchangeable H is simple and accurate. In comparison with other methods employing a buffer medium, Innes and Birch (9) found the BaCl<sub>2</sub>-triethanolamine to replace H efficiently. Its high buffer capacity and sufficiently high pH give good results with soils of the 1:1 and organic types. These types are known to require a higher pH for the effective neutralization of H (18, 21, 28).

The exchangeable Mg is colorimetrically determined. Thiazol yellow, in place of titan yellow, has been adopted following the preliminary report of Mikelsen and Toth (19). Thiazol yellow compared favorably with Grubler's titan yellow. The same concentration previously suggested for titan yellow (16) was found to give satisfactory results. The oxalate and other ions in the filtrate from the Ca determination do not interfere with the test, provided the analysis is made within 24 hours after the filtrate is obtained. The procedure for exchangeable K is virtually the same as that previously described (25). A large number of comparisons of the proposed procedure and that of the ammonium acetate method give nearly identical results. The procedure for exchangeable Na has been adopted in all essential details from that proposed by Peech (24). Determination of K and Na in the BaCl<sub>2</sub>-triethanolamine extract is made much more rapidly and conveniently with the flame photometer after removal of Ba with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Data obtained with these methods are shown in table 1. The results are satisfactory for all practical purposes.

Whenever the sum of cations is appreciably greater than the cation-exchange capacity, the presence of water-soluble salts or of water-soluble carbonates or hydroxides is indicated. In highly unsaturated soils the exchangeable hydrogen may sometimes exceed the cation-exchange capacity. This has been found to be due to free Al-salts. This excess may be corrected by subtracting the aluminum from the hydrogen. The presence of H<sub>2</sub>O-soluble carbonates or hydroxides is

usually suspected whenever, in the titration for hydrogen, negative values are obtained. These negative values may be reported as free alkalis and, when subtracted from the sum of the exchangeable metal cations, yield results that are nearly equivalent to the cation-exchange capacity.

#### *Cation-exchange capacity*

The advantages of the  $\text{BaCl}_2$ -triethanolamine procedure, from the standpoint of its excellent buffer properties, effective replacement of H, favorable comparison with the  $\text{CaCO}_3$ - $\text{CO}_2$  equilibration and  $\text{NH}_4$  volatilization methods, and its adaptability to soils containing carbonates, have been previously discussed (15, 16, 18). The reaction of Ba to form insoluble carbonates when used on calcareous soils has been found of little practical consequence in the presence of triethanolamine buffered at pH 8.1. The use of  $\text{CaCl}_2$  for the replacement of

TABLE 1

*Comparison of the colorimetric and flame photometric methods for potassium and sodium*

SOIL	K ADDED	K FOUND		Na ADDED	Na FOUND	
		Colori- metric	Flame pho- tometric		Colori- metric	Flame pho- tometric
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
Norfolk sand.....	0.0	0.07	0.09	0.0	0.05	0.05
Norfolk sand.....	0.1	0.17	0.18	0.05	0.10	0.09
Norfolk sand.....	0.2	0.29	0.30	0.25	0.27	0.26
Portsmouth fine sandy loam..	0.0	0.05	0.08	0.0	0.04	0.05
Portsmouth fine sandy loam..	0.1	0.15	0.16	0.1	0.14	0.17
Portsmouth fine sandy loam..	0.2	0.26	0.28	0.5	0.47	0.52
Cecil clay loam.....	0.0	0.80	0.81	0.0	..	0.06

Ba reduces further this possibility. The presence of sulfates or finely powdered  $\text{SiO}_2$  was found to yield high results when the Ba adsorbed was determined by difference. The interfering of various substances has been reinvestigated with the modified procedure. The results of this investigation are shown in table 2 together with a study of the adsorption of  $\text{BaOAc}$  and the replacement of Ba by  $\text{N NH}_4\text{OAc}$ .

The results show the adsorption of Ba to be greater from  $\text{BaCl}_2$ -triethanolamine than from the acetate in the case of titanite, ferric phosphate, and silicic acid. The reverse is true for calcium silicate, calcite, apatite, and calcium phosphate. The amounts of Ba replaced by  $\text{NH}_4\text{OAc}$  for most of the minerals are of about the same order for both systems, with the exception of calcium silicate, apatite, and calcium phosphate where the replacement of Ba from  $\text{BaOAc}$  is greater. The amounts of Ba replaced by  $\text{CaCl}_2$  are notably lower in all cases than those replaced by  $\text{NH}_4\text{OAc}$ . Even with this replacement agent, substantial quantities of Ba are recovered from calcite and from ferric and aluminum phosphates.

The results with the proposed procedure may be too low if the amount of



soil sample taken for analysis is represented by appreciably more than 2.5 m.e. cation-exchange capacity. This maximum figure has been derived from extensive experimentation. Some of the results are shown in table 3. The samples used varied appreciably in the amounts of exchangeable cations. For optimum values of the cation-exchange capacity, the results show the need for an amount of solution A to supply Ba equivalent to at least 10 times symmetry. If this requirement is met, satisfactory results for exchangeable cations are obtained.

TABLE 2

*Adsorption of Ba by minerals and chemicals from 0.2 N BaCl<sub>2</sub>-triethanolamine (pH 8.1) and BaOAc (pH 7.0), and replacement of Ba with N NH<sub>4</sub>OAc and 0.6 N CaCl<sub>2</sub>*

MINERAL OR CHEMICAL*	ADSORPTION AND REPLACEMENT OF Ba FROM:				
	BaCl <sub>2</sub> -N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>			BaOAc	
	Ba adsorbed	Replaced by		Ba adsorbed	Replaced by NH <sub>4</sub> OAc
		CaCl <sub>2</sub>	NH <sub>4</sub> OAc		
	m.e./gm.	m.e./gm.	m.e./gm.	m.e./gm.	m.e./gm.
Titanite.....	0.21	0.02	0.14	0.10	0.10
Stibnite.....	0.10	0.003	0.05	0.08	0.04
Spinel.....	0.21	0.006	0.10	0.23	0.06
Bauxite.....	0.16	0.01	0.06	0.14	0.05
Albite.....	0.15	0.005	0.09	0.17	0.10
Stilbite.....	0.15	0.01	0.11	0.15	0.09
Serpentine.....	0.09	0.03	0.05	0.08	0.04
Silicic acid.....	0.12	0.08	0.12	0.07	0.07
Ca-silicate.....	0.86	0.012	0.81	2.46	2.20
Calcite.....	1.60	0.37	1.53	2.00	1.60
Dolomite.....	0.48	0.06	0.40	0.46	0.36
Apatite.....	0.20	0.005	0.08	0.50	0.40
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	0.30	0.006	0.15	1.24	0.60
FePO <sub>4</sub> .....	2.31	0.44	0.69	0.91	0.44
AlPO <sub>4</sub> .....	1.83	0.39	0.55	1.70	0.47

\* The silicic acid, CaSO<sub>4</sub>, Ca-, Fe-, and Al-phosphates are c. p. chemicals: the kaolinite is "Kamec Kaolin" from North Carolina, the Ca-silicate is from the T. V. A., Knoxville, Tennessee, and all others are from Ward's Natural Science Establishment, Rochester, New York.

In practice it was found that a 10-gm. sample is most frequently needed. For sandy soils, low in organic matter, 20 gm. should be used; for organic soils and clays, 5 gm. A correspondingly smaller sample is needed for muck and peat.

Low values for cation-exchange capacity have been occasionally encountered as a result of coadsorption of (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH ions from triethanolamine, notably by soils of the 2:1 lattice type. After some experimentation it was found that washing the soil with 25 ml. of 0.2 N BaCl<sub>2</sub> aided in removing these ions.

The technique proposed for the colorimetric determination of Ba is rapid and accurate. The use of CaOAc as the replacement reagent for Ba, as proposed by Millar *et al.* (20), is not recommended, since it was found to interfere in the pre-



precipitation of  $\text{BaCrO}_4$ . Broadfoot and Tyner (2) encountered similar difficulties. The precipitation of  $\text{BaCrO}_4$  in the presence of  $\text{CaCl}_2$  does not entail any analytical difficulties. The colorimetric determination of Ba as  $\text{BaCrO}_4$  is rapid and accurate.

### *Anion-exchange capacity*

The adsorption of  $\text{PO}_4$  by soil colloids involves several proposed mechanisms (4, 5, 6, 13, 29, 32). There is as yet no agreement as to the definition of anion-

TABLE 3

*Effect of symmetry concentration of Ba on cation-exchange capacity, exchangeable H, Ca, Mg, and K*

SYMMETRY CONCENTRATION*	AMOUNT OF		CATION- EXCHANGE CAPACITY	EXCHANGEABLE			
	Soil†	Solution A		H	Ca	Mg	K
High H; low Ca, Mg, K							
	gm.	ml.	m.e.	m.e.	m.e.	m.e.	m.e.
5	10	50	19.0	18.6	1.33	0.18	0.181
10	10	100	20.8	18.9	1.34	0.19	0.184
20	5	100	20.9	19.1	1.34	0.19	0.184
Medium H, Ca, Mg; low K							
5	10	50	20.1	13.2	7.34	0.42	0.127
10	10	100	21.0	13.9	7.34	0.43	0.129
20	5	100	20.9	14.0	7.35	0.43	0.130
Medium H, Ca; high Mg, K							
5	10	50	20.1	9.7	8.09	1.49	0.394
10	10	100	20.9	10.4	8.06	1.68	0.412
20	5	100	20.9	10.4	8.10	1.77	0.410
High Ca; medium Mg; low H, K							
5	10	50	20.6	3.7	18.10	0.43	0.149
10	10	100	21.1	3.7	18.42	0.44	0.158
20	5	100	20.9	3.8	18.54	0.43	0.154

\* Symmetry concentration expressed in terms of milliequivalents of Ba used in relation to the cation-exchange capacity.

† Portsmouth fine sandy loam, variously treated with Ca, Mg, and K.

exchange capacity. This property is governed by the method employed with special reference to the pH at which the adsorption of  $\text{PO}_4$  is allowed to take place (5, 26, 30). The present procedure differs in that the pH at which the  $\text{PO}_4$  is adsorbed is a variable governed by the type of colloid present or the acidoid-basoid properties of the soil. The pretreatment of the soil is likewise expected to influence the results. Pretreatment with acids or with neutral or hydrolyzable salts invariably leaves a residue containing free salts of Al and Fe. This is par-

ticularly true if the reaction takes place below the ultimate pH of the colloid. In the  $\text{BaCl}_2$ -triethanolamine procedure the final reaction is invariably above the ultimate pH. In fact, it coincides with the isoelectric pH of the Al-basoid (pH 8.1), at which it is amphotERICALLY neutral (13, 14). Since the H ions supplied with  $\text{H}_3\text{PO}_4$  do not exceed the exchangeable Ca (the second and third H in  $\text{H}_3\text{PO}_4$  play a negligible role in this respect), the final pH will remain above the ultimate

TABLE 4  
*Equilibrium pH, cation-exchange:anion-exchange ratio, and anion-exchange capacity of soils and minerals*

SOIL OR MINERAL*	TYPE OF COLLOID	pH <sub>e</sub>	CATION-EXCHANGE: ANION-EXCHANGE RATIO	ANION-EXCHANGE CAPACITY  mmol./100 gm.
Halloysite.....	Halloysite	5.2	1.2	14.9
Indianaite, Ill.....	Halloysite	5.4	1.4	13.5
Kaolin "Kamec", N. C... (18)	Kaolinite	3.9	2.0	4.2
Kaolin, S. C..... (11)	Kaolinite	3.7	2.2	2.0
Durham B horizon, N. C.. (18)	Kaolinite	4.8	1.4	3.7
Cecil B horizon, N. C.... (18)	Kaolinite	4.0	1.7	6.8
Orangeburg Ch horizon, N. C. (3)	Kaolinite	3.7	1.8	2.5
Susquehanna B horizon, N. C..... (3)	Kaolinite-montmorillonite	3.3	2.3	9.5
Grenada A horizon, Miss.. (3)	Beidellite-kaolinite	4.0	1.8	5.4
Houston B horizon, Miss.. (3)	Montmorillonite	3.0	3.8	10.8
Lufkin A horizon, Ala..... (3)	Montmorillonite	2.9	4.2	10.2
Weller 42-51 inches, Iowa. (27)	Montmorillonite	2.9	5.0	6.1
Clarion 49-55 inches, Iowa. (27)	Montmorillonite	2.8	6.7	1.9
Bentonite, Volclay, Wyo.. (10)	Montmorillonite	2.6	20.0	4.5
Bentonite, Miss..... (10)	Montmorillonite	2.6	12.5	6.2
Bentonite, Ortovician... (10)	Montmorillonite-mica	2.6	20.0	1.8
Illite, Ill..... (8)	Mica	2.8	7.1	2.7
Zeo Dur.....	Mica	2.9	5.5	4.3
Collington B horizon, N. J. (18)	Mica	2.9	4.5	6.3
Peat A horizon, Florida... (18)	Organic	2.7	25.0	9.6
Muck A horizon, N. C.....	Organic	2.9	10.0	9.2

\* Figures in parenthesis refer to literature where more detailed information on the mineral or chemical composition and source of soils and minerals may be found.

pH. In this manner, an increase in the positive charge of the basoid, and hence excessive adsorption of  $\text{PO}_4$ , are restricted.

Since the proposed procedure involves an equilibrium reaction and the phosphorus adsorbed is determined by difference, a more accurate measure of anion-exchange capacity is obtained if the  $\text{NH}_4\text{F}$ -replaced  $\text{PO}_4$  is added to the  $\text{PO}_4$  adsorbed. This procedure will correct for the presence of Ca- and Ba-phosphates, which are rendered partly soluble by  $\text{H}_3\text{PO}_4$  and acidified  $\text{NH}_4\text{F}$ . Preliminary tests employing the same relative extraction period as that followed in

the regular procedure have shown the tertiary Ca- and Ba-phosphates to be only slightly more soluble in  $\text{NH}_4\text{F}$  than in  $\text{H}_3\text{PO}_4$ . The acidified  $\text{NH}_4\text{F}$  replacement solution adopted is twice as concentrated as that proposed by Bray.<sup>3</sup> This has been possible since the F ions do not interfere in the colorimetric molybdovanadate method (31) which has been adopted for this purpose.

The anion-exchange capacities of various soils and minerals are presented in table 4. The anion-exchange capacity obtained with this method may be expected to be lower than that obtained with methods employing heat or time treatments of long duration for bringing about phosphorus fixation (26, 30). In the proposed procedure the effect of time on these properties is shown in table 5. It will be noticed that the anion-exchange capacity rose sharply between 2 and 20 hours, but increased only slightly beyond that period. The measurements after 24 hours are fairly constant and reproducible. An extension of contact beyond 2 days is not recommended, since the mixture of Ca-soil and phosphate represents a good growth medium for microorganisms, which would be expected to affect the results.

TABLE 5

*Effect of time of contact of  $\text{H}_3\text{PO}_4$  with bentonite and soils on  $\text{pH}_e$  and anion-exchange capacity*

SOIL	$\text{pH}_e$			ANION-EXCHANGE CAPACITY		
	2 hours' contact	20 hours' contact	44 hours' contact	2 hours' contact	20 hours' contact	44 hours' contact
				mmol./100 gm.	mmol./100 gm.	mmol./100 gm.
Bentonite. ....	2.50	2.55	2.57	0.0	4.5	4.5
Bladen B <sub>2</sub> horizon...	2.96	3.10	3.12	2.4	3.5	3.6
Halewood A horizon.	3.63	4.05	4.13	3.6	5.1	5.1
Davidson A horizon.	4.13	4.70	4.79	7.0	9.6	10.0

The effects of concentration of  $\text{H}_3\text{PO}_4$  on  $\text{PO}_4$  adsorbed and on the cation-exchange capacity of Durham and Cecil soils are shown in figure 1. The  $\text{PO}_4$  adsorbed continues to increase with increasing concentration. After the addition of 1.5 m.e., however, the slope is less steep. The cation-exchange capacity likewise increases with increasing amounts of  $\text{PO}_4$  supplied. Above 1.2 m.e.  $\text{PO}_4$  added, this increase is small. The 1-millimol or 3-m.e. increment of  $\text{PO}_4$  supplied in the recommended procedure is, therefore, sufficient to saturate the easily accessible positively charged exchange positions.

*Characterization of soil colloids by means of the cation-exchange:anion-exchange ratio and equilibrium pH*

Addition of  $\text{H}_3\text{PO}_4$  to a Ca-soil results in partial replacement of Ca by H and adsorption of  $\text{PO}_4$ , probably through exchange of OH groups. The degree to

<sup>3</sup> Bray, R. H. Rapid tests for measuring and differentiating between the adsorbed and acid-soluble forms of phosphate in soils. Mimeographed directions, department of agronomy, Illinois Agricultural Experiment Station, AG1028. 1942.

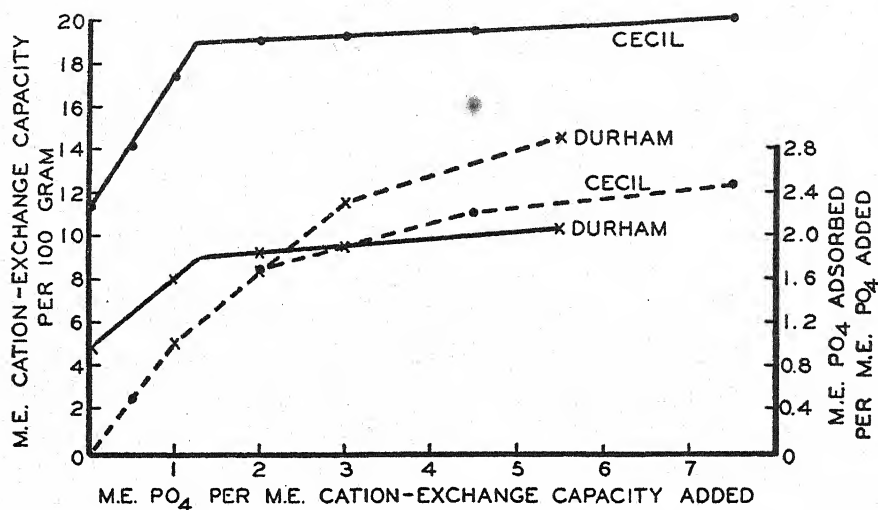


FIG. 1. EFFECT OF ADDING INCREASING AMOUNTS OF  $\text{PO}_4$  TO SOILS ON THE CATION-EXCHANGE CAPACITY (SOLID LINE) AND ON THE  $\text{PO}_4$  ADSORBED (BROKEN LINE)

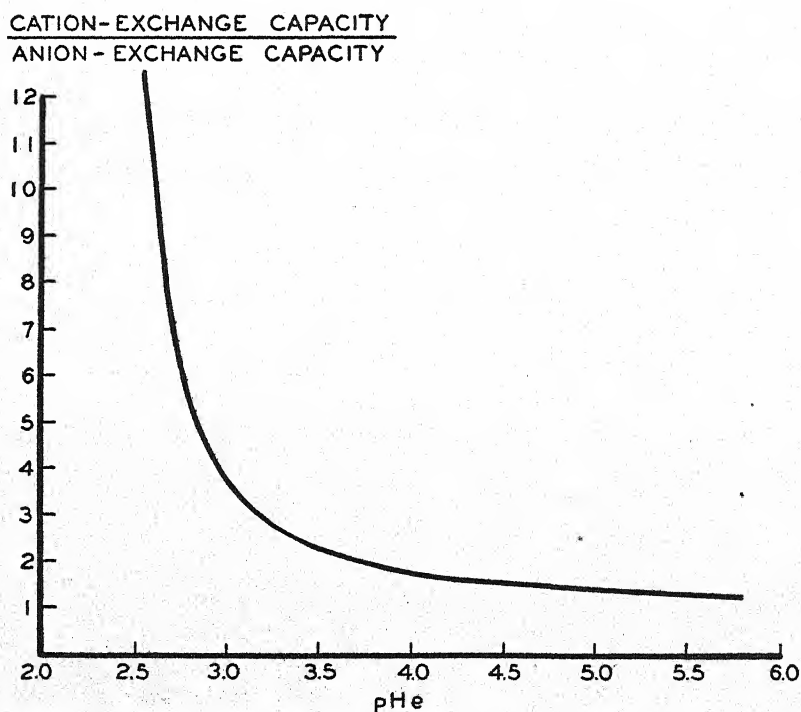


FIG. 2. RELATIONSHIP BETWEEN CATION-EXCHANGE:ANION-EXCHANGE RATIO AND EQUILIBRIUM  $\text{pH}(\text{pH}_e)$

which these reactions occur may be expected to depend on the type of colloid predominating in the soil. The physical and chemical properties of the colloids of the 2:1 and 1:1 mineral lattice type are known to vary widely as a result of their differences in mineralogical and chemical structure (1, 8, 12). Differences in these soil properties affect the equilibrium pH ( $pH_e$ ) as well. The relationship between  $pH_e$  and the cation-exchange/anion-exchange ratio is shown in figure 2. The curve represents the average of a large number of determinations on mineral soils or colloids. For soils with organic matter the curve would be shifted somewhat to the right, denoting a higher  $pH_e$  for any given cation-exchange:anion-exchange ratio. Since the organic fraction is known to react with the mineral colloid (7, 22), it is probable that substitution of the OH groups by the organic colloid is involved, but that the substituted groups are not easily replaceable by the  $PO_4$  and F ions. An alternate possibility is the partial interaction of the organic fraction with the mineral colloid through cation-exchange (7). This would result in a lowering of the cation-exchange:anion-exchange ratio; hence, in an increase in  $pH_e$ .

The effect of type of colloid on  $pH_e$ , cation-exchange:anion-exchange ratio, and anion-exchange capacity is shown in table 4. There are appreciable variations within each group of soils or minerals containing a predominant type of colloid. In general,  $pH_e$  is highest and the cation-exchange:anion-exchange ratio is lowest in halloysite, followed by kaolinite and the bentonites. The soils containing predominating montmorillonite and the micas exhibit lower exchange ratios than those of the bentonites. The exchange ratios for the organic soils are also high.

The proposed procedure for the chemical characterization of soil colloids has the advantage of simplicity and convenience of operation. It is less time-consuming and virtually as simple as the methods employing the base saturation-pH relationship (17). The equilibrium pH, cation-exchange:anion-exchange ratio, and exchangeable  $PO_4$  values may be expected to be useful in various problems of plant nutrition, notably in connection with problems of liming and Ca availability.

#### SUMMARY

Methods for determining exchangeable H, Ca, Mg, K, Na,  $PO_4$ , soluble Al, cation and anion-exchange capacities of soils have been described. In carrying out the procedure, enough air-dry soil to give 0.5 to 2.5 m.e. exchange capacity is weighed into special funnels,  $BaCl_2$ -buffered at pH 8.1 with triethanolamine added, washed with unbuffered  $BaCl_2$ , and finally with  $H_2O$ .

Aliquots of the filtrate are taken for the determination of exchangeable H, Ca, Mg, K, and Na. For H, a simple titration procedure is used. Calcium is determined volumetrically with  $KMnO_4$  in the presence of  $BaSO_4$ , and Mg is determined colorimetrically with thiazol yellow. For determination of K and Na, Ba is first removed as the carbonate, and K and Na are estimated either colorimetrically or with the flame photometer.

The cation-exchange capacity is obtained by replacement of Ba from the soil



with  $\text{CaCl}_2$ , precipitating the Ba as the chromate, and finally determining  $\text{BaCrO}_4$  colorimetrically. For determination of anion-exchange capacity the Ca-saturated soil is treated with  $\text{H}_3\text{PO}_4$  in an amount equivalent to the cation-exchange capacity. After 24 hours of contact, the pH is measured, and the  $\text{PO}_4$  adsorbed is determined. The exchangeable  $\text{PO}_4$  is determined by replacement with acidified  $\text{NH}_4\text{F}$ .

Brief studies are reported on some factors influencing the results. It was shown that replacement of Ba with  $\text{CaCl}_2$  rendered only small amounts of Ba soluble when present in nonexchangeable form, as compared to its replacement with  $\text{NH}_4\text{OAc}$ . The exchange capacity is, therefore, not affected by the presence of  $\text{CaCO}_3$  or  $\text{MgCO}_3$  in soils, which are but slightly soluble in the buffered extract.

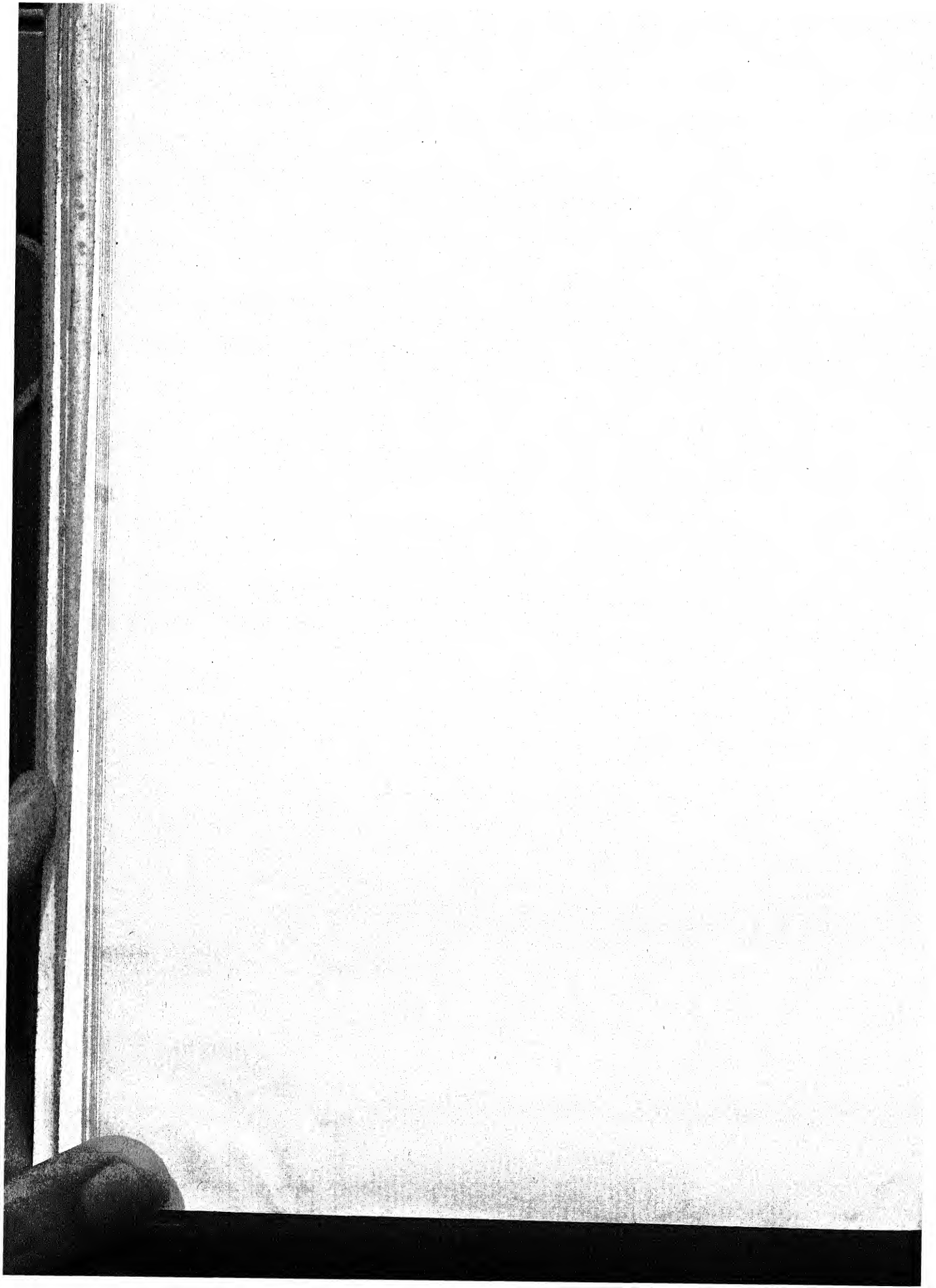
It was found that the addition of 1 millimol or 3 m.e. of  $\text{H}_3\text{PO}_4$  per milliequivalents cation-exchange capacity as recommended in the procedure is sufficient to saturate the larger portion of the easily accessible bonds which are concerned in cation and anion-exchange reactions.

The equilibrium pH ( $\text{pH}_e$ ) and the cation-exchange:anion-exchange ratios were found to serve as a qualitative measure for distinguishing between mineral colloids of the 2:1 and 1:1 lattice types.

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# A COMPARISON OF AMMONIUM ACETATE AND BUFFERED BARIUM CHLORIDE METHODS FOR DETERMINING CATION-EXCHANGE PROPERTIES OF LIMED SOILS<sup>1</sup>

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Workers in soil science are frequently presented with the problem of selecting a method for determining the cation-exchange properties of soils. One of the most widely used methods in the eastern United States involves the use of ammonium acetate. Mehlich (2) pointed out the disadvantages of ammonium acetate for determining cation-exchange properties of soils the colloid fraction of which was primarily of the organic or kaolinitic type. In addition, solubility of calcium carbonate in ammonium acetate limits the value of the acetate in determining exchangeable calcium in recently limed soils. In proposing the use of buffered barium chloride, Mehlich emphasized its advantages on limed soils and on soils the colloid fraction of which was of the organic or kaolinitic type. The purpose of this study was to investigate the buffered barium chloride method more fully, and to compare it with the ammonium acetate method, on soils that had received recent additions of lime.

## PROCEDURE

### *Soil from field plots*

Soil samples were taken from field experiments designed to study the effect of degree of base saturation on growth and development of soybeans.<sup>2</sup> Samples were taken from three fields in the lower coastal plain area of North Carolina. The soil types involved were Craven very fine sandy loam, Bladen silt loam, and Hyde sandy loam; the predominate types of colloid in these soils were kaolinite, montmorillonite-organic mixture, and organic, respectively.

The design of the experiment on these fields, so far as base saturation treatments were concerned, was a 3 by 3 balanced lattice with four replications of nine treatments. The plots consisted of five 3-foot rows each 46 feet long. The soil treatments consisted of additions of calcitic and dolomitic limes and gypsum calculated to give base saturations ranging from 6 to 90 per cent of the cation-exchange capacity. The amounts of materials applied and the degree of base saturation that these were designed to give are shown in table 1.

The lime and gypsum applications were made in March 1945. In addition, all plots received a uniform application of  $MgSO_4$  as a sidedressing in May 1945

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<sup>2</sup> These experiments are under the supervision of W. L. Nelson. The authors are indebted to him for permission to sample these plots and for assistance given in this study.



at a rate to supply 50 pounds of MgO per acre. The soils were sampled prior to planting in April 1946.

Determinations for pH were made with a glass electrode assembly. Cation-exchange capacity and exchangeable calcium and magnesium were determined by the ammonium acetate procedure as outlined by Peech *et al.* (4) and by the buffered barium chloride method proposed by Mehlich (3). Exchangeable hydrogen was also determined by this method, and in the case of the ammonium acetate method it was computed as the difference between the exchange capacity and the sum of the metal cations. The amount of residual carbonate in limed samples was determined by the method of Schollenberger (5).

TABLE 1  
*Soil treatments and degrees of base saturation designed*

TREATMENT NUMBER	TYPE OF MATERIAL	BLADEN SILT LOAM		CRAVEN VERY FINE SANDY LOAM		HYDE SANDY LOAM	
		Treatment	Theoretical saturation	Treatment	Theoretical saturation	Treatment	Theoretical saturation
		lb./A.	per cent	lb./A.	per cent	lb./A.	per cent
1	.....	0	15	0	15	0	6
2	Calcitic lime	2,420	30	885	30	3,150	20
3	Calcitic lime	7,200	60	2,650	60	7,650	40
4	Calcitic lime	11,400	90	4,420	90	16,500	80
6	Gypsum	15,400	60	6,050	60	17,300	40
7	Dolomitic lime	1,730	30	665	30	2,610	20
8	Dolomitic lime	5,170	60	2,000	60	5,840	40
9	Dolomitic lime	8,600	90	3,320	90	12,700	80

*Rate of reaction study in the laboratory*

Further to compare the two methods on recently limed soils, samples of the untreated Bladen and Craven soils were used for laboratory lime treatments. Samples of 300 gm. of soil were placed in 400-ml. beakers, and lime was added to give 90 per cent saturation if all reacted. Two of the treatments involved dolomitic limestone ( $\text{CaCO}_3$ -52 per cent,  $\text{MgCO}_3$ -37 per cent) of two levels of fineness: (a) that fraction passing through a 2-mm. sieve but remaining on a 100-mesh screen, and (b) that passing through a 100-mesh screen. Two other treatments included the use of precipitated calcium carbonate and calcium hydroxide. In addition to these treatments, 300-gm. samples from the field treatments originally designed to provide 90 per cent base saturation in these two soils were also placed in 400-ml. beakers. All treatments were in duplicate.

The moisture equivalent was determined for these soils, and the samples in the beakers were maintained at a moisture level of two thirds of these values for 2 months. After 1 month and 2 months, samples were taken with a  $\frac{1}{4}$ -inch cork borer and determinations made of pH, exchangeable calcium, magnesium, and hydrogen, and residual carbonates. Exchangeable cations were determined by the buffered barium chloride method.



## RESULTS AND DISCUSSION

In connection with the use of a barium salt for determining cation-exchange capacity, it has been found by other workers that increasing amounts of Ba from BaOAc are adsorbed by soils as the pH increases upon the addition of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ . This was recently pointed out by Davis (1). Indications are, however, that with  $\text{BaCl}_2$ -triethanolamine, the cation-exchange capacity is not affected by pH or the presence of  $\text{CaCO}_3$ . Data illustrating this are shown in table 2, which contains comparison with the BaOAc method on soils differing in their predominant type of colloid.

TABLE 2

*Influence of reaction and type of colloid on cation-exchange capacity and exchangeable H as measured by the  $\text{BaCl}_2$ -triethanolamine and BaOAc methods*

SOIL	TYPE OF COLLOID PREDOMINATING	pH	CATION-EXCHANGE CAPACITY		EXCHANGEABLE H	
			$\text{BaCl}_2$	BaOAc	$\text{BaCl}_2$	BaOAc
			m.e.*	m.e.	m.e.	m.e.
White Store.....	2:1	4.6	25.7	26.5	18.5	18.2
White Store.....	2:1	8.2	26.5	28.5	0.0	0.0
Putnam.....	2:1	5.1	63.0	62.0	28.0	27.5
Putnam.....	2:1	8.5	64.0	74.0	0.0	0.0
Collington.....	Hydrous mica	4.7	24.0	24.5	18.5	14.2
Collington.....	Hydrous mica	8.5	24.5	29.0	0.0	0.0
Cecil.....	1:1	4.7	13.6	11.0	10.7	5.4
Cecil.....	1:1	8.0	13.2	16.0	0.7	0.0
Durham.....	1:1	4.8	14.2	13.0	11.5	9.8
Durham.....	1:1	8.5	14.8	17.5	1.0	0.0
Portsmouth.....	Organic	5.0	19.2	19.2	15.0	11.0
Portsmouth.....	Organic	8.5	19.6	25.0	1.5	0.0
Peat.....	Organic	4.8	236.0	212.0	140.0	90.0
Peat.....	Organic	8.7	240.0	253.0	0.0	0.0

\* m.e. = per 100 gm. soil.

The cation-exchange capacity by the BaOAc method, in comparison with that by the  $\text{BaCl}_2$  method, is greater for soils above pH 8, containing  $\text{CaCO}_3$ , than for the soils of lower pH. The cation-exchange capacity and the exchangeable H are about the same with both salts for  $\text{CaCO}_3$ -free soils of the 2:1 lattice type; but for  $\text{CaCO}_3$ -free soils of the organic and 1:1 lattice type, the values of the BaOAc method are lower. These data further support the contention that variations in the type of colloid and exchangeable H yield more consistent results when the replacement medium employed is well buffered. Both the organic and the 1:1 lattice type of colloids require a higher pH for neutralization of H. Since the BaOAc is but slightly buffered above pH 6, its effectiveness in neutralizing H depends on the concentration of the salt and the hydroxyl ion produced on hydrolysis. For the same reason, large amounts of Ba are adsorbed in non-

exchangeable form by alkaline or calcareous soils, and these amounts will vary with the concentration of the salt.

*Comparison of methods on limed soils from field*

*Cation-exchange capacity and exchangeable hydrogen.* Values for cation-exchange capacity and for exchangeable hydrogen for the three soils by the two methods are listed in table 3. Each value represents the mean of duplicate determinations on each of four replications. There were some soil variations among replications, and these were naturally reflected in the exchange capacities. How-

TABLE 3

*Cation-exchange capacity and exchangeable hydrogen of limed soils as measured by  $\text{NH}_4\text{OAc}$  and  $\text{BaCl}_2$ -triethanolamine methods*

Average of duplicate determinations on four replications

THEORETICAL SATURATION*	TYPE LIME	BLADEN SILT LOAM				CRAVEN FINE SANDY LOAM				HYDE SANDY LOAM†			
		Exchange capacity		Exchange $\text{H}^+$		Exchange capacity		Exchange $\text{H}^+$		Exchange capacity		Exchange $\text{H}^+$	
		$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$	$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$	$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$	$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$	$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$	$\text{BaCl}_2$	$\text{NH}_4\text{OAc}$
per cent		m.e.†	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
15	None	22.1	14.1	16.7	10.3	9.5	4.3	5.2	3.1	38.2	17.2	35.2	12.9
30	Calcitic	22.7	13.1	14.7	6.7	10.2	6.3	6.0	3.9	38.7	17.1	29.2	8.7
30	Dolomitic	24.0	15.1	16.5	9.9	10.1	6.1	6.9	3.5	40.2	21.9	28.4	10.8
60	Calcitic	22.3	14.2	9.6	3.8	10.0	5.0	2.5	0	39.2	18.9	20.1	3.1
60	Dolomitic	21.2	13.5	9.8	4.9	9.5	5.6	3.7	1.0	35.2	18.8	19.8	4.9
60	Gypsum	22.4	13.7	14.7	5.6	9.7	5.5	6.5	2.1	38.1	17.9	33.0	3.5
90	Calcitic	22.1	14.7	6.0	0.4	10.0	5.5	0.8	0	35.9	20.0	8.2	0
90	Dolomitic	22.4	14.9	6.1	1.2	9.6	5.6	1.7	0	38.7	16.9	11.4	0
L.S.D... (0.05)		1.5		2.2		1.6		1.6		6.1		4.3	
L.S.D... (0.01)		2.1		3.0		2.1		2.2		8.3		5.9	

\* Values given are for Bladen and Craven soils.

† Theoretical degrees of saturation for the Hyde soil were 6, 20, 20, 40, 40, 80, and 80 per cent, respectively.

‡ m.e. = per 100 gm. soil.

ever, the purpose of this study was to compare the methods rather than to study differences in exchange capacity within a soil area.

In all samples from the three soils, values for cation-exchange capacity determined by the buffered barium chloride method are considerably higher than those for the ammonium acetate method. Differences in cation-exchange capacity values by the two methods are partly explained by the differences in amounts of exchangeable hydrogen found by the two methods. Exchangeable hydrogen determined by the buffered barium chloride is consistently higher than that determined with ammonium acetate by difference. The differences between the exchangeable hydrogen values for buffered barium chloride and those for am-

monium acetate may be obtained. If these are added to the ammonium acetate exchange capacity values, they give values for the exchange capacity which more nearly approach the barium chloride values. Since the two extractants are buffered at different reactions, a difference in amount of hydrogen by the two methods is to be expected on soils the base saturation-pH curves of which do not reach a maximum at or below pH 7.0. Mehlich (2) has shown that the efficiency of ammonium acetate in replacing hydrogen is much less than that of buffered barium chloride at both pH 6.0 and pH 7.0 with a number of soils.

Exchangeable hydrogen content of all soils decreases with increase in amount of liming materials added, except in the case of gypsum where hydrogen content at a theoretical base saturation of 60 per cent (40 per cent on Hyde soil) is approximately equal to the hydrogen at the 30 per cent (20 per cent on Hyde soil) level with calcitic and dolomitic limes.

In a number of cases with the ammonium acetate method, where hydrogen was calculated as the difference between exchange capacity and exchangeable calcium and magnesium, no exchangeable hydrogen is indicated. Most of these are samples which had received the highest additions of lime. In the data from which these mean values were obtained there were twelve instances in which no hydrogen was found even though the pH was 6.7 or below. It is possible that electrometric titration of the ammonium acetate extract would yield higher values for hydrogen in some cases, especially those in which it is apparent that the ammonium acetate is dissolving some of the free carbonate. On one gypsum plot of the Hyde soil the pH was 4.6, even though the ammonium acetate method did not show any exchangeable hydrogen. This was probably due to inability of the ammonium acetate to replace all the hydrogen and to solution of unreacted calcium sulfate by the ammonium acetate.

The data indicate that lime treatments had no effect on cation-exchange capacity as measured by either method on any of the three soils. This is as might be expected of the ammonium acetate procedure in view of investigations by other workers. It would be expected of the barium chloride method on the basis of the data presented in table 2. Mehlich (2) has shown that basic salts are not formed in the buffered barium chloride procedure. There is also apparently no interference from free carbonates in the buffered barium chloride procedure. It is possible that barium carbonate may be formed and precipitated in the soil during leaching with the barium chloride solution; yet there is no evidence that decomposition of the barium carbonate is effected by the calcium chloride leaching, since the soils receiving highest additions of lime and still containing free carbonates (table 4) do not show higher values for exchange capacity.

*Exchangeable calcium and magnesium.* Further explanation of differences between buffered barium chloride and ammonium acetate values for exchange capacities of the Bladen and Craven soils comes from a study of the amounts of exchangeable calcium and magnesium found by the two methods. Mean values for these are contained in table 4. There is some evidence that at the lower base saturations in these two soils the ammonium acetate was not so effective as the barium chloride in replacing calcium. If the calcium was not being replaced,

TABLE 4

*Properties of limed soils as determined by the  $\text{NH}_4\text{OAc}$  and  $\text{BaCl}_2$ -triethanolamine methods*

THEORETICAL SATURATION	TYPE LIME	CALCIUM		MAGNESIUM		SATURATION		pH	RESIDUAL CARBONATES
		BaCl <sub>2</sub>	NH <sub>4</sub> OAc	BaCl <sub>2</sub>	NH <sub>4</sub> OAc	BaCl <sub>2</sub>	NH <sub>4</sub> OAc		
Bladen silt loam									
per cent		m.e.*	m.e.	m.e.	m.e.	per cent	per cent		m.e.
15	None	3.8	3.3	0.6	0.5	20.0	27.0	4.7	0.4
30	Calcitic	6.2	5.6	0.8	0.8	30.5	48.9	5.0	1.3
30	Dolomitic	5.2	3.6	1.6	1.5	28.8	33.7	5.0	0.6
60	Calcitic	10.2	9.8	0.9	0.7	49.7	73.4	5.8	1.9
60	Dolomitic	7.2	6.1	4.0	2.5	55.4	63.6	5.8	1.5
60	Gypsum	6.5	7.6	0.7	0.5	31.9	60.1	4.6	0.8
90	Calcitic	13.6	15.6	0.7	0.6	64.4	112.1	6.4	3.6
90	Dolomitic	9.6	9.8	5.4	3.9	67.4	94.0	6.4	2.3
L.S.D..... (0.05)		1.7		0.6		12.9			
L.S.D..... (0.01)		3.3		0.8		17.4			
Craven fine sandy loam									
15	None	1.9	0.9	0.3	0.3	23.6	27.5	4.8	0.3
30	Calcitic	3.2	2.1	0.3	0.4	33.8	38.7	5.3	0.5
30	Dolomitic	3.1	1.9	0.8	0.8	38.2	45.5	5.3	0.5
60	Calcitic	5.2	5.9	0.3	0.3	55.0	125.9	6.8	2.3
60	Dolomitic	4.1	3.6	1.6	1.5	59.8	100.1	6.5	1.4
60	Gypsum	3.7	3.2	0.3	0.2	41.4	62.3	4.8	0.6
90	Calcitic	7.1	9.1	0.3	0.3	74.7	173.7	7.2	4.1
90	Dolomitic	5.5	5.6	2.1	2.1	79.5	138.6	7.0	2.8
L.S.D..... (0.05)		1.2		0.8		20.8			
L.S.D..... (0.01)		1.7		1.0		28.2			
Hyde sandy loam									
6	None	3.2	3.8	0.4	0.5	9.1	25.5	4.2	0.3
20	Calcitic	7.3	7.6	0.6	0.8	21.3	50.0	4.9	1.2
20	Dolomitic	7.1	7.6	3.9	3.4	28.3	52.4	5.3	1.6
40	Calcitic	14.9	15.1	0.5	0.7	39.4	84.5	5.6	2.6
40	Dolomitic	9.0	9.3	5.4	4.6	39.8	73.7	5.7	1.8
40	Gypsum	10.1	13.7	0.6	0.8	28.2	81.3	4.3	0.7
80	Calcitic	21.9	25.1	1.3	1.9	65.9	138.7	6.6	10.4
80	Dolomitic	12.2	15.8	9.0	6.7	59.3	134.7	6.6	6.6
L.S.D..... (0.05)		2.7		1.4		15.1			
L.S.D..... (0.01)		3.7		1.8		20.3			

\* m.e. = per 100 gm. soil.



then the ammonium ion was not being adsorbed, and the exchange capacity values would be lowered. On the Hyde soil, however, where differences in exchange capacity between the two methods were even greater, there was no consistent difference in exchangeable calcium or magnesium between the methods of replacement at the lower levels of base saturation.

The amounts of exchangeable calcium and magnesium in all soils increased with increase in amount of lime added. The exchangeable calcium in the gypsum-treated plots for all soils by the barium chloride method was lower than the exchangeable calcium of plots to which equivalent amounts of calcium were added as calcitic lime. In the Bladen and Craven soils the exchangeable calcium of the gypsum plots was comparable to that of plots the treatment of which was designed to give 30 per cent base saturation. This was also true of the exchangeable hydrogen of these plots.

Another characteristic of the buffered barium chloride in measuring only exchangeable bases is evident in the difference in the amount of calcium removed by the two methods from the samples that had received the highest amounts of calcitic lime. The ammonium acetate consistently extracted more calcium from these samples than did the barium chloride, even though at lower levels of saturation the ammonium acetate extracted less. It is probable that this increase in extraction by the ammonium acetate is due to the solution of residual calcium carbonate.

*Base saturation and pH.* Percentage base saturation (table 4) determined by the barium chloride method is in fair agreement with the theoretical degree of saturation for the first two increments of lime on all soils, indicating that these two increments of lime have fully reacted with the soil. This is supported by the data on residual carbonates, which show that only small amounts of lime remain unreacted on these treatments. Most of the variation that occurs between the theoretical and the actual degree of saturation on these plots, especially on the Hyde soil, can be explained by the differences in exchange capacity between plots. Lime additions were made on the basis of an average value for exchange capacity and exchangeable bases of the soils before treatment. The four replications of each treatment, therefore, received equal amounts of lime regardless of their previous status.

At the highest level of theoretical saturation, the desired degree of saturation has not been reached except in a few instances. Either the lime remains in the soil in a nonexchangeable form, or it has been lost through leaching. The amount of residual carbonates remaining in these plots indicates that part of the lime is still present but has not reacted with the soil. Small particles of lime were clearly visible in the dark-colored Bladen and Hyde soils. There is no evidence from the data for exchangeable calcium and magnesium or percentage base saturation that the buffered barium chloride solution dissolved any appreciable amount of either calcium or magnesium carbonates.

The base saturation percentages determined by the ammonium acetate method are considerably higher than those of the barium chloride method. At the lower levels of saturation this is due to the lower exchange-capacity values for ammo-



nium acetate. On the gypsum and high-lime treatments, the increased amount of calcium extracted by the ammonium acetate is an additional cause for the higher percentage base saturation.

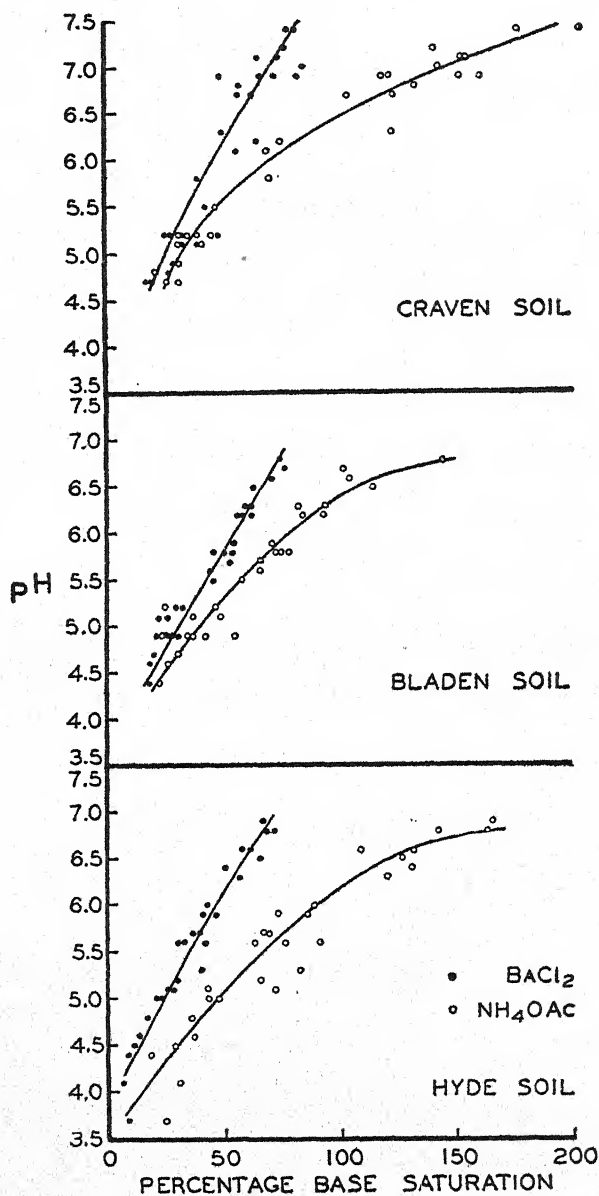


FIG. 1. RELATIONSHIP BETWEEN pH AND BASE SATURATION OF THREE SOILS DETERMINED BY TWO METHODS

A graphic comparison of the relation between base saturation and pH of the three soils is shown in figure 1. In all three cases relationship is not so well

established with the ammonium acetate values. These values also indicate saturation at pH 6.5 or less. At high degrees of base saturation, the ammonium acetate extracted greater amounts of bases than the amount of  $\text{NH}_4$  adsorbed in some cases, so that the apparent base saturation is greater than 100 per cent.

*Residual carbonates.* The amounts of free carbonates in the soils are also shown in table 4. Analyses were made only on samples from the second and third replications for each soil.

The small quantity of carbonates apparently present in the samples receiving no additions of lime may be explained as an error due to the presence of adsorbed  $\text{CO}_2$  or bicarbonates in the soil.

It might be assumed from the data that where free carbonates are present, the soil is saturated with bases, and that the ammonium acetate values for base saturation are more nearly correct than the barium chloride values. It is more likely, however, that the presence of carbonates merely indicates that the lime was not thoroughly mixed with the soil when added, and that sufficient time has not elapsed for complete reaction to take place.

Where the amount of free carbonates present exceeds 4.0 m.e. per 100 gm. on the Bladen and Hyde soils, or 2.0 m.e. per 100 gm. on the Craven soil, the ammonium acetate extraction indicates more than 100 per cent base saturation, and the quantity of exchangeable bases is greater than for the barium chloride extraction. This indicates that some of the carbonates were dissolved by the ammonium acetate but not by the barium chloride.

*Study of rate of reaction in the laboratory.* Laboratory studies were designed to follow the changes in exchangeable hydrogen, exchangeable cations, and residual carbonates in limed soils. Samples of soils were used from the field plots of the Bladen and Craven soils that had been limed theoretically to 90 per cent saturation. In the case of the Craven soil, these contained no exchangeable hydrogen according to the ammonium acetate procedure and were well over 100 per cent saturated. Yet the barium chloride method indicated the presence of exchangeable hydrogen.

These soils were intimately mixed and the properties determined by the  $\text{BaCl}_2$  method as they were and after being maintained at constant moisture for 1 and 2 months. The results are given in table 5. Two points of interest should be emphasized. First, the exchangeable hydrogen decreased with time, and there were corresponding increases in the exchangeable Ca and Mg and corresponding decreases in the residual carbonates. This is further evidence of the advantages of the barium chloride method of studying the exchangeable hydrogen status in limed soils. A second point of interest is the rather rapid reaction of the residual carbonates upon intimate mixing and maintenance at constant moisture. It had been 14 months from the time that lime was applied in the fields until the soil samples were taken, yet a considerable amount of carbonates remained unreacted in the soil. After only 1 month in the laboratory were the remaining carbonates reduced to a very small quantity.

In addition to these studies on soils limed in the field, samples from unlimed plots of these Bladen and Craven soils were treated with various limes in the laboratory. These limes were intimately mixed with the soil and maintained at

TABLE 5

*Rate of reaction and exchangeable cations in previously limed soils after intimate mixing and maintenance in laboratory at constant moisture*

PREVIOUS TREATMENT*	pH			EXCHANGEABLE												RESIDUAL CARBONATES		
				Hydrogen			Calcium			Magnesium								
	Start	1 mo.	2 mo.	Start	1 mo.	2 mo.	Start	1 mo.	2 mo.	Start	1 mo.	2 mo.	Start	1 mo.	2 mo.			
<i>Bladen silt loam</i>																		
				m.e.†	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.		
Calcitic lime....	6.4	6.5	7.2	6.0	3.5	3.4	13.6	19.1	19.3	0.7	1.2	1.4	3.5	0.4	0.8			
Dolomitic lime..	6.3	6.2	6.8	6.1	4.4	4.1	9.6	12.8	13.0	5.4	5.1	5.2	2.3	1.0	1.4			
<i>Craven very fine sandy loam</i>																		
Calcitic lime....	7.2	7.2	7.4	0.8	0.2	0.1	7.1	8.3	8.8	0.3	0.7	0.7	4.0	1.5	1.3			
Dolomitic lime..	7.0	6.8	6.8	1.7	0.7	1.1	5.5	6.7	6.5	2.1	2.3	2.5	2.7	0.6	0.6			

\* Soils from treatments 4 and 9 (table 1) that had been limed to provide theoretically 90 per cent base saturation in March 1945.

† m.e. = per 100 gm. soil.

TABLE 6

*Rate of reaction and exchangeable cations in soils after liming, intimate mixing and maintenance in laboratory at constant moisture*

TREATMENT	Ca ADDED*	Mg ADDED*	pH		EXCHANGEABLE						RESIDUAL CARBONATES	
					Hydrogen		Calcium		Magnesium			
			1 mo.	2 mo.	1 mo.	2 mo.	1 mo.	2 mo.	1 mo.	2 mo.	1 mo.	2 mo.
Bladen silt loam												
	m.e.†	m.e.			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
None.....	0.0	0.0	4.7	...	16.7	...	3.8	...	0.6	...	0.4	...
Dolomite												
Fine.....	8.5	7.2	6.0	6.1	5.5	4.4	11.0	12.4	5.1	6.0	4.7	3.2
Coarse.....	8.5	7.2	5.2	5.4	8.8	8.0	9.1	10.7	3.4	3.9	9.2	6.5
CaCO <sub>3</sub> .....	15.6	0.0	6.5	6.5	3.3	3.0	18.9	18.8	0.5	0.8	0.7	0.7
Ca(OH) <sub>2</sub> .....	11.7	0.0	6.0	6.0	6.0	5.5	15.0	16.2	0.7	0.7	0.6	1.1
Craven very fine sandy loam												
None.....	0.0	0.0	4.8	...	5.2	...	1.9	...	0.3	...	0.3	...
Dolomite												
Fine.....	3.7	2.6	6.2	6.6	2.0	1.5	4.8	5.4	2.7	3.0	1.7	1.6
Coarse.....	3.7	2.6	5.4	5.8	3.0	2.6	3.7	4.3	1.4	2.1	3.9	3.2
CaCO <sub>3</sub> .....	6.3	0.0	7.3	7.3	0.1	0.2	7.9	8.1	0.7	0.5	0.2	0.3
Ca(OH) <sub>2</sub> .....	5.0	0.0	6.4	6.4	1.7	1.9	6.0	6.2	0.3	0.5	0.3	0.3

\* The amounts of Ca and Mg added were designed to provide 90 per cent saturation, except in the case of Ca(OH)<sub>2</sub>, of which enough was added to provide 72 per cent saturation.

† m.e. = per 100 gm. soil.

constant moisture as with those discussed above. The type of lime used and the amounts are listed in table 6 along with the change in soil properties at the end of 1- and 2-month periods.

Here also is illustrated the usefulness of the barium chloride method with limed soils. As the exchangeable hydrogen decreases, the exchangeable bases increase and residual carbonates decrease.

The data in table 6 show that the rate of reaction of the various limes with the Bladen and Craven soils was rapid during the first month. About 75 per cent of the fine dolomite and 50 per cent of the coarse dolomite had reacted on both soils. Complete reaction of both the  $\text{CaCO}_3$  and  $\text{Ca}(\text{OH})_2$  occurred during the first month. At the end of 2 months the fine dolomite was about 90 per cent reacted, and the coarse dolomite 65 per cent, on both soils.

Information on the extraction of calcium and magnesium by buffered barium chloride from soils containing carbonates is also given in tables 5 and 6. The sum of the exchangeable calcium and magnesium in the soil before treatment, plus the amount added, should equal the sum of the exchangeable calcium and magnesium after reaction, plus any remaining carbonate. If the latter sum should be higher, solution of carbonates is indicated. The data show that the difference between the two sums for the dolomite treatments is less than 1.0 m.e. per 100 gm. on both soils, hence the solution of carbonates is small.

#### SUMMARY

The chief objection to the use of  $\text{BaOAc}$  for determining cation-exchange capacity has been that increasing amounts of Ba are adsorbed by soils as the pH increases upon addition of lime. Comparisons of the  $\text{BaOAc}$  method with a method using  $\text{BaCl}_2$  buffered with triethanolamine showed that with the latter method the exchange capacity is not affected by pH or the presence of  $\text{CaCO}_3$ . To compare the  $\text{BaCl}_2$  method with the  $\text{NH}_4\text{OAc}$  method, determinations were made of exchange properties of limed soils of various types.

Samples were taken in April 1946 from field plots of Bladen, Craven and Hyde soils which had been variously treated with calcitic and dolomitic hydrated limes and gypsum. The treatments were designed to give base saturations of 15, 30, 60, and 90 per cent on the Bladen and Craven soils, and 6, 20, 40, and 80 per cent on the Hyde soil. Cation-exchange properties and residual carbonates were determined for these soil samples by means of both barium chloride-triethanolamine and neutral ammonium acetate procedures.

Values for cation-exchange capacity varied widely. The buffered barium chloride procedure gave higher values at all degrees of base saturation with all soils. Most of the variation in cation-exchange capacities between the two procedures could be explained on the basis of differences in amounts of exchangeable hydrogen measured by the two procedures. The amounts of exchangeable hydrogen determined with barium chloride were consistently higher than those for ammonium acetate.

The amounts of exchangeable calcium and magnesium increased with increasing amounts of lime added. On samples at the lower degrees of base saturation,



the amounts of calcium and magnesium extracted by the ammonium acetate were about the same or were slightly less than the amounts extracted by the barium chloride. At the higher degrees of saturation and on most of the gypsum-treated plots, the amounts of calcium extracted by the ammonium acetate procedure were generally considerably higher than the amounts extracted by the buffered barium chloride. The results show that appreciable amounts of calcium carbonate were dissolved by the ammonium acetate but not by the barium chloride solution.

A closer relationship exists between degree of base saturation and pH when determined by the buffered barium chloride procedure than when determined by ammonium acetate.

Samples of the Bladen and Craven soils, which had received no previous treatment, were mixed intimately in the laboratory with various limes in amounts designed to produce approximately 90 per cent base saturation. Rate of reaction of the limes with the soils at constant moisture content was measured by means of the buffered barium chloride procedure and by determinations of pH and residual carbonates. The results showed that the amount of carbonate dissolved by buffered barium chloride was small. As the residual carbonates decreased in these soils, there were a corresponding decrease in exchangeable hydrogen and an increase in exchangeable bases, as measured by the buffered barium chloride method.

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# RAPID QUANTITATIVE DETERMINATION OF EIGHT MINERAL ELEMENTS IN PLANT TISSUE BY A SYSTEMATIC PROCEDURE INVOLVING USE OF A FLAME PHOTOMETER

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Studies being carried out in this laboratory have necessitated development of a rapid and systematic procedure for the quantitative estimation of Ca, Na, K, Mg, Fe, Mn, P, and S in plant tissue. The methods are simple in operation and reliable, and the eight elements can be determined on samples of 1 to 2 gm.

The dry plant tissue is wet-ashed successively with nitric and perchloric acids, the silica is removed by filtration, and the solution is made up to volume. This is designated as solution A, and contains the eight elements that are subsequently to be determined.

Ca, Na, and K are determined on a suitable aliquot of solution A by the use of a flame photometer. Phosphorus is determined colorimetrically as the reduced phosphomolybdate complex on the aliquot of the solution that is used for the determination of Ca, Na, and K by the flame photometer. Manganese is determined colorimetrically as permanganic acid on a separate aliquot of solution A after oxidation with periodate. Iron is determined as the ferrous ortho-phenanthroline complex on a separate aliquot. Sulfur is precipitated and weighed as BaSO<sub>4</sub> on another aliquot. Magnesium is determined colorimetrically with thiazol yellow as a colored Mg-lake, after the removal of R<sub>2</sub>O<sub>3</sub> and Ca.

With the exception of the flame photometer technique for Ca, Na, and K, the procedures are not new but are merely adaptations or modifications of published methods for each element. The analytical scheme and methods employed in this laboratory are described in the following section without comment, and a separate section is devoted to special precautions and techniques.

## INSTRUMENTS AND ANALYTICAL PROCEDURES

A Perkin-Elmer flame photometer, model 52 A, equipped with the acetylene burner and supplied with interchangeable red and blue photocells is used for determination of Ca, Na, and K. A Lumetron photoelectric colorimeter equipped with suitable glass filters and supplied with two types of cells is used for the colorimetric measurements. More recently a Beckman spectrophotometer has been substituted for the colorimeter.

Table 1 contains data on the photocells used for determination of Ca, Na, and K, and on the wave bands, cell dimensions, and ranges for all of the methods employed in the system. The procedure is described in terms of a single determination of each element on one 2-gm. sample.

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*Preparation of solution A*

Weigh a 2-gm. sample of oven-dried plant tissue into a 200-ml. tall Griffin Pyrex beaker. Add 10-15 ml. concentrated nitric acid, cover with a watch glass, and heat gently on a hot plate until no visible signs of solid material remain. At this point the solution is generally straw-colored. Remove the beaker from the hot plate, add 5 ml. 70 per cent perchloric acid, replace the watch glass, and gently boil until clear and fuming with copious vapors of perchloric acid. Generally the volume at this point is about 1-3 ml. Avoid allowing the solution to go to dryness. Add 25 ml. distilled water, bring to a boil, and pass through a Whatman No. 40 filter paper into a 100-ml. volumetric flask. Wash silica with hot water to about 75 ml. Cool, dilute to 100 ml., and label as *solution A*. Discard the dehydrated silica.

TABLE 1  
*Data on methods used*

ELEMENT	RANGE OF METHOD	TISSUE IN ALIQUOT	VOLUME OF SOLUTION A	FILTER USED	CELL WIDTH	METHOD
	mgm.*	mgm.	ml.	mμ.	cm.	
Ca	0.06-6.0	200†	10†	...	...	Flame photometer-blue photocell
Na	0.02-2.0	200†	10†	...	...	Flame photometer-blue photocell
K	0.06-6.0	200†	10†	...	...	Flame photometer-red photocell
Mg	0.2-2.0	200	10	500	2.0	Thiazol yellow
Fe	0.0005-0.03	100	5	530	2.0	Ortho-phenanthroline
Mn	0.001-0.05	500	25	530	2.0	Periodate
P	0.001-0.06	4†	2.5†	660	1.0	Reduced phosphomolybdate
S	1-10	1000	50	...	...	BaSO <sub>4</sub>

\* As used in schematic procedure (mgm.) in plant tissue.

† Same aliquot for Ca, Na, K, and P.

*Flame-photometer determinations for Ca, Na, and K*

Pipette 10 ml. solution A into a 100-ml. volumetric flask, add 10 ml. 250-p.p.m. LiCl solution, and dilute to 100 ml. The solution is now ready for the determination of Ca, Na, and K.

*Calcium.* Warm up the flame photometer containing the blue photocell for at least  $\frac{1}{2}$  hour prior to its use. Locate the position of the Ca line on the wavelength scale with a solution containing 60 p.p.m. Ca in the form of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . With the location established, reset the machine for the indirect method of determination, using 25 p.p.m. Li in the form of the chloride as the internal standard. Set the 60 p.p.m. Ca solution containing 25 p.p.m. Li at 100, and check one point on the curve to be sure that the machine is working satisfactorily. A 30-p.p.m. Ca solution should read 50 scale divisions when the 60-p.p.m. Ca solution is set at 100. Pour unknowns in the funnel of the flame photometer

and record scale readings:  $\frac{\text{p.p.m.}}{20} = \text{per cent Ca.}$

*Sodium.* Locate the position of the Na line on the wavelength scale using a solution containing 20 p.p.m. Na in the form of NaCl. With the location established, reset the machine for the indirect method of determination, using 25 p.p.m. Li in the form of the chloride as the internal standard. Set the 20-p.p.m. Na solution containing 25 p.p.m. Li at 100, and check one point on the curve. A 10-p.p.m. Na solution should read 52 scale divisions when the 20-p.p.m. Na solution is set at 100. Pour unknowns into the funnel of the flame photometer and record scale readings. Read parts per million Na from curve:

$$\frac{\text{p.p.m.} - \text{correction for Ca}}{20} = \text{per cent Na.}$$

*Potassium.* Remove the blue photocell from the instrument and replace with the red photocell. Warm up the flame photometer and locate the position of the K line on the wavelength scale with a solution of 60 p.p.m. K in the form of KCl. With the location established, reset the instrument for the indirect method of determination, using 25 p.p.m. Li in the form of the chloride as the internal standard. Set the 60-p.p.m. K solution containing 25 p.p.m. Li at 100, and check one point on the curve. A 30-p.p.m. K solution should read 43 scale divisions when the 60-p.p.m. K solution is set at 100. Pour unknown into the funnel of flame photometer and record scale reading. Read parts per million K from standard curve:  $\frac{\text{p.p.m.}}{20} = \text{per cent K.}$

#### *Colorimetric determinations*

*Phosphorus* is determined by an adaptation of the methods of Fiske and Subbarow (2) and Chapman (1).

Pipette a 2-ml. aliquot of the solution used for the flame-photometer determination of Ca, Na, and K into a 50-ml. volumetric flask. Dilute to approximately 25 ml. with distilled water; add 2.2 ml. 2.5 per cent ammonium molybdate solution in 10 N H<sub>2</sub>SO<sub>4</sub>.<sup>2</sup> Make up to volume, shake well, and add 0.25 ml. of freshly prepared 1 per cent stannous chloride solution.<sup>3</sup> Prepare a set of standards simultaneously. Allow the color for each sample to develop for 15 minutes and read in a photoelectric colorimeter, using a filter of 660 mμ wavelength for color comparison.

*Magnesium* is determined with thiazol yellow as a colored Mg-lake (4), after removal of R<sub>2</sub>O<sub>3</sub> and Ca.

Pipette a 10-ml. aliquot of solution A into a 250-ml. beaker, dilute to 50 ml., add 2 drops of methyl red indicator, and precipitate the R<sub>2</sub>O<sub>3</sub> by adding 1+1 NH<sub>4</sub>OH to the boiling solution. Boil for 1 minute and filter. Redissolve the R<sub>2</sub>O<sub>3</sub> precipitate in 1+1 HCl, dilute with water, and reprecipitate R<sub>2</sub>O<sub>3</sub> as before. Filter and wash precipitate with hot 2 per cent NH<sub>4</sub>NO<sub>3</sub> solution. Acidify com-

<sup>2</sup> Dissolve 25 gm. c.p. ammonium molybdate in 200 ml. distilled water, heat to 60°C., and filter. Cool, and pour into 280 ml. of concentrated H<sub>2</sub>SO<sub>4</sub>. Cool to room temperature and dilute to 1,000 ml.

<sup>3</sup> Place 0.25 gm. of stannous chloride in a 25-ml. volumetric flask, add 10 ml. of concentrated HCl, heat until dissolved, cool, and dilute to volume.

bined filtrates with HCl, and precipitate Ca as oxalate by adding 5 ml. saturated  $(\text{NH}_4)_2 \text{C}_2\text{O}_4$  solution and 1+1  $\text{NH}_4\text{OH}$  until methyl red indicator turns yellow. Boil to granulate precipitate, allow to stand for 1 hour on hot plate, and filter. Redissolve the oxalate precipitate and reprecipitate as before. Wash second precipitate with hot water until free of oxalate. Discard the precipitate.

To combined filtrates add 40 ml. concentrated  $\text{HNO}_3$ . Evaporate to dryness and bake on hot plate to remove  $\text{NH}_4$  salts.<sup>4</sup> Digest with hot water plus 2.5 ml. 1+1 HCl. Filter if necessary, and make to volume of 100 ml.

Pipette a 10-ml. aliquot into a 50-ml. volumetric flask, add 20 ml. distilled water, and then add in the following order: 1 ml. 2 per cent starch solution,<sup>5</sup> 1 ml. 5 per cent hydroxylamine hydrochloride solution, 0.5 ml. 0.10 per cent aqueous solution of Thiazol yellow, and mix thoroughly; and then add 2 ml. 3N NaOH solution. Make to volume, mix thoroughly, and allow to stand for exactly 20 minutes. Prepare a set of standard solutions simultaneously. Read in a spectrophotometer at a wavelength of 500  $\text{m}\mu$  and slit width of 0.04 mm., using a 1-cm. cell or a colorimeter employing a filter near 500  $\text{m}\mu$ .

*Manganese* is determined colorimetrically as the permanganic acid after oxidation with periodate. The procedure is an adaptation of that of Willard and Greathouse (8).

Pipette a 25-ml. aliquot of solution A into a 125-ml. Erlenmeyer flask, add 3 ml. syrupy phosphoric acid (85 per cent), evaporate to fuming perchloric fumes on hot plate, and continue heating until most of the fumes have been removed. Cool, dilute to about 25 ml. with water, add from 0.2 to 0.4 gm.  $\text{KIO}_4$ , and bring to a boil on a hot plate. Continue heating until the maximum color develops, and finally place on steam bath for 1 hour. Cool and dilute to 25 ml. Prepare a set of standards simultaneously and read in a photoelectric colorimeter, using a filter of 530  $\text{m}\mu$  wavelength for color comparison.

*Iron* is determined colorimetrically as the ferrous ortho-phenanthroline complex (6).

Pipette a 5-ml. aliquot of solution A into a 25-ml. volumetric flask, add 0.5 ml. 5 per cent solution of hydroxylamine hydrochloride and 1 ml. 0.20 per cent solution ortho-phenanthroline in 25 per cent alcohol. Mix and add a sufficient quantity of 60 per cent ammonium acetate solution to obtain complete color development. Dilute to volume. Prepare a set of standards simultaneously and read on a photoelectric colorimeter, using a filter of 530  $\text{m}\mu$  wavelength for color comparison. The color should be read within 1 hour after its development.

*Sulfur* is determined gravimetrically, by precipitation and weighing as  $\text{BaSO}_4$ .

Pipette a 50-ml. aliquot of solution A into a 250-ml. beaker. Dilute to 200 ml., bring to a boil on a hot plate, and slowly add 5 ml. of a hot 10 per cent  $\text{BaCl}_2$  solution. Allow the precipitate to become granular by placing on a steam bath for at least 4 hours. Allow to stand overnight and pass the  $\text{BaSO}_4$  through a Whatman No. 44 filter paper. Ignite and weigh as  $\text{BaSO}_4$ .

<sup>4</sup> In some cases it may be necessary to flame the beakers to remove the last traces of ammonium salts.

<sup>5</sup> Freshly prepared, boiled, and filtered soluble starch solution.



*Precautions in technique*

The usual precautions that are observed in colorimetric and gravimetric procedures should be adhered to in the determination of Fe, Mn, P, and S. The colorimetric procedure listed for Mg in the previous section must be strictly followed, especially with respect to time and to the addition of the various reagents.

Calcium is the first element to be determined by the flame photometer, since its presence in solution exerts an influence on the determination of Na. With a knowledge of the Ca concentration in the extract, a proper correction is applied to the determined Na values to get the true values. Calcium and K values, as determined, are not affected by the normal ions that are encountered in plant-tissue digests, and Na is influenced only by Ca.

Since Ca, Na, and K are determined on the same solution, it is desirable to prepare a set of standard curves for routine use such that the majority of the tissues analyzed will automatically fall on some point on them. This is of importance, since all three elements in the scheme can ordinarily be determined without further dilution of the aliquot.

After a study of the experimental data and a review of the literature on the chemical composition of plants, standard curves for Ca, Na, and K were prepared, using 60, 20, and 60 p.p.m. of the cations, respectively, as the highest values. The concentrations listed for the elements correspond to 3, 1, and 3 per cent of Ca, Na, and K, respectively, when a tissue aliquot of 200 mgm. diluted to a volume of 100 ml. is used. The content of Ca, Na, and K in most plant samples will be covered by these ranges. With plant tissue that is abnormally low in Ca it is necessary to increase the size of the aliquot. If the readings on unknowns are above the maximum ranges listed for each element, smaller aliquots must be used for the analysis.

Studies of the standard curves for Ca, Na, and K in the presence of ions normally found in plant tissue have shown that when the concentrations of 3, 1 and 3 per cent of these elements, respectively, in an aliquot corresponding to 200 mgm. of dry plant tissue are used, the curves for Ca and Na are linear but the K curve is not. The Na curve, as pointed out previously, is influenced by the concentration of Ca in the solution; therefore, it is necessary to correct for the presence of this element. The Na curve does not pass through the 0 point of the intersection of the ordinate and abscissa, but intersects the ordinate at a point equivalent to a reading of 4 scale-units. With increasing concentrations of Ca, the curve tends to be identical to that obtained in the absence of Ca, and to parallel it. The shift of the curve is a function of the Ca content of the solution. In the presence of 60 p.p.m. Ca, the curve intersects the ordinate at a point corresponding to a scale reading of 8. If Na readings corresponding to 8 scale-units are obtained on a solution containing 60 p.p.m. Ca, the value for Na is not significant. Calcium, up to concentration of 60 p.p.m., does not influence the K curve. It is necessary, however, to read K values directly from the standard K curve, since the relation between concentration and scale reading is not linear. The Ca curve is not influenced by the presence of up to 20 p.p.m. Na or 60 p.p.m. K.



The choice of the internal standard method of procedure for the determination of Ca, Na, and K is based upon the fact that it is not necessary to control rigidly either the gas and air pressure or the acidity of the extracts. The viscosity differences due to changes in acidity and salt content do not significantly influence the rate of atomization. The 25 p.p.m. Li, as the chloride, for the internal standard was selected as the result of exhaustive tests to establish the best concentration of the internal standard suitable for most types of plant tissue. It is possible that other concentrations of the internal standard may be better suited for certain types of plant tissue.

It is essential that the position of the wavelength scale for each of the three elements concerned be determined each time the instrument is used, since there is a tendency for the position of the wavelengths to shift slightly on the scale. At least two points must be established on the curve for each cation to ensure that the instrument is working satisfactorily. Experience has shown that three readings must be obtained for each cation on unknown samples, with adequate checking of the 0 point of the galvanometer after each three readings. It is also important that the null point of the galvanometer be set with distilled water passing through the atomizer.

#### RESULTS AND DISCUSSION

The proposed system of analysis for eight elements in plant tissue, especially the flame-photometer techniques for Ca and K, have been thoroughly checked against standard methods of analysis for these elements. The data indicate excellent agreement between both procedures. Typical results for Ca and K are presented in table 2. Values for Na, by standard methods of analysis, are not recorded in table 2, since it is believed that values so obtained are not so reliable as those determined by use of the flame photometer (7). The speed of analysis and the adaptability of the flame-photometer techniques for routine use in plant analysis make this procedure far superior to standard procedures for the three cations. Once the technique of operation of the instrument is acquired, it is possible for an operator to obtain Ca, Na, and K values of an average plant-tissue digest in less than 30 minutes.

The system of analysis of plant tissue outlined for the eight elements has been in use in these laboratories for some months, and excellent results have been obtained. Success with the procedure and speed of analysis depend upon the proper utilization of the time factor for determination of each element. Since certain of the procedures are adaptations of gravimetric and colorimetric methods, it is essential that they be placed in operation before the shorter methods are initiated. For example, preliminary steps in the determination of S, Mn, and Mg can be set up prior to making the flame photometer determinations of Ca, Na, and K or the colorimetric determination of Fe and P. The analysis of 50 tissue samples for the eight elements mentioned can be easily performed in 48 hours. This is of special interest, since microchemical methods for the cations are not used in the system.

The reliability of the procedures used is indicated by the data in table 3.

Varying amounts of the eight elements were added to four different types of plant tissue before digestion, and the percentage recovery of each was determined. Simultaneously, tissue samples without the addition of the elements were analyzed. The data represent the average values of duplicate samples. The re-

TABLE 2

*Comparison of standard procedures of analysis for Ca and K and flame photometric values*

TISSUE	Ca			K			Na FLAME
	Volumetric* Method	Flame	Difference	Gravimetric† Method	Flame	Difference	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Bean pods.....	0.61	0.60	-0.01	1.93	1.93	0.00	0.03
Lettuce.....	0.79	0.80	+0.01	...	2.35	...	0.05
Spinach.....	2.02	1.99	-0.03	4.68	4.68	0.00	0.98
Bean tops.....	0.48	0.50	+0.02	3.97	3.90	-0.07	0.03
Lettuce #135.....	0.39	0.39	0.00	...	...	...	0.05
Spinach.....	1.93	1.95	+0.02	9.98	10.00	+0.02	0.45

\* Precipitation as oxalate and subsequent titration with standard  $\text{KMnO}_4$ .

† As  $\text{K}_2\text{PtCl}_6$ .

TABLE 3

*Determination of calcium, potassium, sodium, sulfur, phosphorus, manganese, iron, and magnesium on four types of plant tissue with added increments of these elements*

TISSUE	Ca				K				Na				S			
	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>
Radish Tops.....	10.0	41.5	41.6	100.2	10.0	64.5	65.7	101.8	5.0	5.3	5.2	98.1	2.5	11.6	11.6	100.0
Lettuce....	10.0	17.9	17.4	97.2	10.0	76.5	75.0	98.0	5.0	10.6	10.6	100.0	2.5	6.1	5.8	95.0
Carrot Roots.....	10.0	12.4	11.9	96.0	10.0	34.5	35.7	103.5	5.0	9.3	9.2	98.9	2.5	4.0	3.9	97.5
Bean Top.....	10.0	18.3	17.8	97.2	10.0	39.7	39.0	99.5	5.0	5.2	5.3	101.9	2.5	4.4	4.3	97.7
Average.....	....	....	....	97.6	....	....	....	100.7	....	....	....	99.9	....	....	....	97.5
TISSUE	P				Mn				Fe				Mg			
	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery	Added	Total present	Found	Recovery
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>
Radish Tops.....	2.8	9.2	9.6	104.3	0.50	0.595	0.584	98.1	0.245	1.200	1.300	108.3	2.0	6.0	5.9	98.3
Lettuce.....	2.8	9.1	9.5	104.3	0.50	0.580	0.568	98.9	0.245	1.235	1.270	102.8	2.0	5.8	5.6	96.5
Carrot Roots.....	2.8	6.7	7.2	107.4	0.50	0.518	0.504	97.2	0.245	0.410	0.410	100.0	2.0	4.4	4.4	100.0
Bean Top.....	2.8	5.3	5.7	107.5	0.50	0.522	0.500	96.0	0.245	0.470	0.497	105.7	2.0	8.0	8.3	103.7
Average.....	....	....	....	105.8	....	....	....	97.3	....	....	....	104.2	....	....	....	99.6

covery of Ca ranged from 96.0 to 100.2 per cent. The mean recovery was 97.6 per cent.

Recovery of K ranged from 98.0 to 103.5 per cent. The mean recovery averaged 100.7 per cent. Unlike the microchemical methods that have been proposed for K in plant tissue (3), it is not necessary to follow any system of precipitating

complex insoluble salts of K, which are of variable composition depending on the conditions under which the precipitation is carried out.

Recovery of Na ranged between 98.1 and 101.9 per cent. The mean recovery amounted to 99.9 per cent. The Na content of plant tissue is not commonly reported in the literature, since the usual methods of estimating this element are time-consuming and unreliable.

Recovery of S ranged between 95.0 and 100.0 per cent. The mean recovery amounted to 97.5 per cent.

The mean recovery of P amounted to 105.8 per cent. Two factors may be responsible for this high recovery: silica is not completely removed in the procedure, and only a very small aliquot is used for the analysis.

Recovery of Mn ranged between 96.0 and 98.9 per cent. The mean recovery amounted to 97.3 per cent.

Recovery of Fe, like that of P, was somewhat high. The mean amounted to 104.2 per cent.

Recovery of Mg ranged between 96.5 and 103.7 per cent. The mean recovery amounted to 99.6 per cent. The use of thiazol yellow, rather than titan yellow, in the estimation is of considerable interest, since the range of sensitivity of the former is from 1 to 10 p.p.m. whereas with the latter it is only from 1 to 3 p.p.m. Mg. Recent studies have shown that  $R_2O_3$  and Ca, which interfere in Mg determinations and must be removed, can be precipitated as insoluble tungstates (5). This results in greatly speeding up the determination of Mg by the thiazol yellow method.

From the foregoing data, it will be noted that recoveries of added increments of eight elements to four types of plant tissue were excellent. The best recoveries were obtained with Ca, K, Na, S, Mn, and Mg, but those of P and Fe were entirely satisfactory for a rapid system of analysis.

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## BOOKS

*Advances in Food Research.* Volume 1. Edited by E. M. MRAK AND GEORGE F. STEWART. Academic Press, Inc., New York, 1948. Pp. 459. Price \$7.50.

Reports on investigations in the field of food research are so widely scattered among a considerable series of journals that it seemed advisable to develop a means by which they could be reviewed on a continuing basis. That is the reason for the publication of this volume. It will be followed by others. The current volume reviews the literature on physiology and chemistry of rigor mortis, factors affecting the vitamin content of canned foods, physiological basis for voluntary food intake, biochemical factors influencing the shelf life of dried whole eggs, factors affecting the palatability of poultry, deterioration of processed potatoes, influence of climate and fertilizers on vitamin and mineral content of vegetables, nonenzymatic browning in fruit products, microbial inhibition by food preservatives, and high-polymer pectins and their deesterification. Most of the chapters are well illustrated and they are followed by lists of 100 or more references. Judging by the first volume, the series will be highly useful in meeting an important need to workers in this field of research.

*Bibliography of the Literature on the Minor Elements and their Relation to Plant and Animal Nutrition.* Fourth Edition. Volume 1. Chilean Nitrate Educational Bureau, Inc., New York, 1948. Pp. 1037.

In the preparation and publication of this volume, the Chilean Nitrate Educational Bureau, under the direction of Dr. Herbert C. Brewer, has rendered an exceptional service to all those who are concerned with minor elements in plant and animal nutrition. References to the literature on 45 elements are presented. This volume represents much careful reviewing on the part of a number of qualified persons, beginning with the pioneering efforts of Dr. L. G. Willis of the North Carolina Agricultural Experiment Station. It covers the work of some 4,500 research specialists and makes it possible for the reader to gain, within a few minutes, a relatively good idea of the extent to which any one of these elements has been found to affect plants and animals. The thanks of a great many persons are due the Bureau for this monumental contribution to the literature in this highly important field.

*Bibliography of the Literature on Sodium and Iodine, in Relation to Plant and Animal Nutrition.* Volume 1. Chilean Nitrate Educational Bureau, Inc., New York, 1948. Pp. 123.

As the title indicates, the purpose of this volume is to present abstracts of the literature on the experimental work with sodium and iodine in relation to their usefulness to plants and animals. The work of some 750 scientists is reviewed. Virtually all the crops from alfalfa to vetch are covered. Under general nutri-



tion are included birds, cats, cattle, dogs, fish, frogs, goats, guinea pigs, horses, poultry, rabbits, reptiles, rodents, sheep, and swine. The publication of this volume should lead to renewed interest in these two elements, which merit much further study.

*Farm Soils, Their Management and Fertilization.* Fourth Edition. By EDMUND L. WORTHEN. John Wiley and Sons, Inc., New York, 1948. Pp. 510, figs. 100. Price \$3.20.

Written primarily for farmers and for such others as are directly concerned with the practical business of growing crops, this book begins with a discussion of the problem of selecting a farm. It then offers suggestions on growing the crop, draining and irrigating, controlling erosion, tiling, manuring, liming, fertilizing, and supplying organic matter. Finally the management problem is considered in relation to field crops, pastures, gardens, greenhouses, lawns, and fruits. Some 30 years of extension experience in New York State, on top of some 15 years of previous experience in Illinois, the U. S. Bureau of Soils, North Carolina, and Pennsylvania, have gone into the preparation and revision of the book.

*Grass, the Yearbook of Agriculture, 1948.* Edited by ALFRED STEFFERUD. U. S. Government Printing Office, Washington, D. C. Pp. 892. Price \$2.

This volume consists of a series of 137 papers on "Grass in the Nation's Life," each prepared by a specialist or specialists in the particular phase of the subject. The introduction deals with grass in permanent agriculture. This is followed by consideration of grass in conservation, for livestock, in rotations, for the range, and in relation to the economy of the several regions of the United States. The volume is well illustrated and contains, in addition to the usual black and whites, 32 photographs in color. Appended are lists of scientific and common names of plants and some 600 references. This is an exceptionally important and useful reference volume, which should be readily available to all those concerned with the development of a better agriculture in this country.

*Land Economics.* Edited by ROLAND R. RENNE. Harper and Brothers, New York, 1947. Pp. 725, figs. 48. Price \$5.

This book deals with the land resources of the United States. It gives the background and perspective, discusses principles, presents the major land uses, outlines policies, and offers suggestions on the planning and control of land use. The illustrations are well chosen and are very helpful in understanding the text. References to supplemental reading are appended to the chapters, and many others are given at the bottoms of the several pages, together with many interesting notes that aid in understanding the text. The presentation is lucid. The author has a wide grasp of the subject. All those who have to do with agricultural, forest, recreational, urban, or mineral lands, or with water resources or transportation, will find this a valuable reference volume.

*Machines for the Farm, Ranch and Plantation.* By ARTHUR W. TURNER AND ELMER J. JOHNSON. McGraw-Hill Book Co., Inc., New York, 1948. Pp. 793, figs. 778. Price \$4.80.

In this exceptionally well prepared and well illustrated book, all types of machines for use on the farm are described and pictured. The groupings are: seedbed-preparation machines, crop-planting machines, crop-tillage machines, harvest and harvest-handling machines, mechanical power and transportation machines, general service machines, and barn and product equipment. The material is presented on the basis of job activity. Included are discussions of special machines for crop conditioning, crop protection, soil conservation with regular farm machinery, nut-gathering, and bulb-harvesting. A list of visual aids is appended to the book. Excellent illustrations are an outstanding feature.

*Précis des Découvertes et Travaux Somnologiques.* By C. S. RAFINESQUE-SCHMALTZ. Peter Smith, 321 Fifth Ave., New York, 1948. Pp. 55. Price \$4.

This is a reprint, in an edition of only 350 copies, of a book originally published in 1814 and of which only six copies are recorded in American libraries. The last copy, offered for sale in 1947, was priced at \$250. In a foreword to the reprint, Dr. E. D. Merrill, Director of the Arnold Arboretum of Harvard University, writes: "In spite of the brevity . . . , this little work is and always will be basic in reference to taxonomic studies of both plants and animals. In it appear descriptions of 110 new species of animals . . . and 79 new species of plants."

*Proceedings of the Twenty-Third Annual Meeting of the National Joint Committee on Fertilizer Application.* Compiled under the direction of J. B. Hester, Arthur W. Turner, and F. S. Lodge, through the assistance of the National Fertilizer Association. Washington, D. C. Pp. 276.

This is a paper-bound, multigraphed report of the 23rd annual meeting that was held in Chicago, December 15, 1947, together with reports of collaborators in studies on fertilizer application. The American Society of Agricultural Engineers, American Society of Agronomy, American Society of Horticultural Science, Farm Equipment Institute, National Fertilizer Association, and National Canners Association are represented in this organization. The report gives further evidence of the very constructive joint effort that has gone into the study of the problems involved in application of fertilizers for best crop results.

*Some Elements of Plants and Animals.* By FRANK EWART CORRIE. Fertilizer Journal, Ltd., London, 1948. Pp. 116. Price 8/6.

This book consists of a series of articles which appeared in the *Fertilizer and Feeding Stuffs Journal* during the years 1945-1947. The author's interest is primarily that of the relation of mineral elements to animal nutrition and health.

In the preparation of the original articles some 3,000 documents were examined from which a list of 226 references was prepared. The first 13 chapters deal individually with as many elements, including not only those normally supplied by lime and fertilizers but also sodium, chlorine, iron, iodine, copper, manganese, cobalt, and boron. The last chapter covers zinc, molybdenum, fluorine, silicon, selenium, and nickel. The author has rendered a highly useful service to his colleagues in this field.

*Weather Elements.* Third edition. By THOMAS A. BLAIR. Prentice-Hall, Inc., New York, 1948. Pp. 373, figs. 112. Price \$5.65.

Rapid developments in the science have necessitated extensive revision in the third edition of this textbook in elementary meteorology. The material is presented in an interesting and attractive manner. A set of questions is appended to each chapter. The chapters on world weather relationships and on the United States Weather Bureau are of special interest. The appendix contains a well-developed bibliography of over 100 publications, conversion factors and tables, tables from Fahrenheit to Centigrade and *vice versa*, and mean monthly and annual temperatures and precipitation. The book is well illustrated and meets admirably the purposes for which it was intended.

THE EDITORS.

## AUTHOR INDEX

- Allison, F. E. *See* Pinck, L. A.  
 Attoe, O. J. *See* Evans, C. E.  
 Barshad, I. Molybdenum in pasture plants, 187-195.  
 Bingham, F. *See* Jenny, H.  
 Bouyoucos, G. J., and Mick, A. H. Measuring soil moisture, 217-232.  
 Bower, C. A., and Huss, R. B. Estimating gypsum in soils, 199-204.  
 Bray, R. H. Chemical soil tests, 83-89.  
 Brennan, E. G. *See* Leone, I. A.  
 Brennan, E. G., and Shive, J. W. Calcium and boron nutrition of tomato, 65-75.  
 Carolan, R. Determining soil organic matter, 241-247; influence of heating on pH of soil suspensions, 417-420.  
 Clements, L. B. *See* MacIntire, W. H.  
 Daines, R. H. *See* Leone, I. A.  
 Dalton, F. H., and Hurwitz, C. Sterilization of soil, 233-238.  
 DeRigo, H. J. *See* Newman, A. S.  
 DeRose, H. R. *See* Newman, A. S.  
 Edgington, G. *See* Robinson, W. O.  
 Evans, C. E., and Attoe, O. J. Potassium-supplying power of soils, 323-334.  
 Fried, M. *See* Wear, J. I.  
 Fripiat, J. *See* D'Hoore, J.  
 Fujimoto, C. K., and Sherman, G. D. Behavior of manganese in soil, 131-145.  
 Gaddy, V. L. *See* Pinck, L. A.  
 Gardner, W. H. Determining the critical stream, 205-215.  
 Giesecking, J. E. *See* Wiklander, L.  
 Hanna, W. J., and Reed, J. F. Determining cation-exchange properties of limed soils, 447-458.  
 Hardin, L. J. *See* MacIntire, W. H.  
 D'Hoore, J., and Fripiat, J. Structure of Yangambi soils, 91-104.  
 Hopp, H., and Slater, C. S. Earthworms and soil productivity, 421-428.  
 Hurwitz, C. Availability of soil manganese, 267-272; *see* Dalton, F. H.  
 Huss, R. B. *See* Bower, C. A.  
 Jenny, H. Soil groups in equatorial regions of Colombia, 5-28.  
 Jenny, H., Bingham, F., and Padilla-Saravia, B. Equatorial soils of Colombia, 173-186.  
 Karim, A. Decomposition of water hyacinth, 401-416.  
 Krishna, P. G., and Perumal, S. Structure in black cotton soils, 29-38.  
 Leone, I. A., Brennan, E. G., Daines, R. H., and Robbins, W. R. Fluorine absorption by plants, 259-266.  
 Lucas, R. E., Copper in organic soils, 119-129.  
 MacIntire, W. H., Winterberg, S. H., Hardin, L. J., Sterges, A. J., and Clements, L. B. Synthetic organic phosphates, 249-257.  
 Martin, J. P. Seedling growth in old citrus soils, 273-288.  
 Mehlich, A. Cation- and anion-exchange properties of soils, 429-445.  
 Mehlich, A., and Reed, J. F. Cation content of plants, 289-306.  
 Mehring, A. L. Magnesium in fertilizers, 147-159.  
 Mick, A. H. *See* Bouyoucos, G. J.  
 Mikkelsen, D. S. *See* Toth, S. J.  
 Mikkelsen, D. S., Toth, S. J., and Prince, A. L. Determination of magnesium, 385-392.  
 Mooers, C. A., Washko, J. B. and Young, J. B. Soil mulches, moisture, and nitrates, 307-315; effect of straw mulch on nitrogen recovery, 399-400.  
 Newman, A. S., DeRose, H. R., and DeRigo, H. T. Persistence of a herbicide in soils, 393-397.  
 Nikiforoff, C. C. Stony soils and their classification, 347-363.  
 Padilla-Saravia, B. *See* Jenny, H.  
 Perumal, S. *See* Krishna, P. G.  
 Pinck, L. A., Allison, F. E., and Gaddy, V. L. Utilization of nitrogen in cropping systems, 39-52.  
 Prince, A. L. *See* Mikkelsen, D. S.; Toth, S. J.  
 Pripiat, J. *See* D'Hoore, J.  
 Reed, J. F. *See* Hanna, W. J.; Mehlich, A.  
 Retzer, J. L. Soils developed from basalt, 365-375.  
 Richards, L. A. Measuring moisture in soil, 105-110.  
 Robbins, W. R. *See* Leone, I. A.  
 Robinson, W. O. Molybdenum in phosphate rock, 317-322.

- Robinson, W. O., and Edgington, G. Toxic aspect of molybdenum in vegetation, 197-198.
- Schaller, F. W. Boron in West Virginia soils, 335-346.
- Sherman, G. D. *See* Fujimoto, K.
- Shive, J. W. *See* Brennan, G.
- Slater, C. S. *See* Hopp, H.
- Steckel, J. E. *See* Wear, J. I.
- Sterges, A. J. *See* MacIntire, W. H.
- Toth, S. J. *See* Mikkelsen, D. S.
- Toth, S. J., Prince, A. L., Wallace, A., and Mikkelsen, D. S. Determining mineral elements in plants, 459-466.
- Wallace, A. *See* Toth, S. J.
- Washko, J. B. *See* Mooers, C. A.
- Wear, J. I., Steckel, J. E., Fried, M., and White, J. L. Clay mineral models, 111-117.
- White, J. L. *See* Wear, J. I.
- Wiklander, L., and Gieseking, J. E. Exchangeability of adsorbed cations, 377-384.
- Winterberg, S. H. *See* MacIntire, W. H.
- Woodruff, C. M. Testing soils for lime requirement, 53-63.
- Young, J. B. *See* Mooers, C. A.



## SUBJECT INDEX

- Absorption—  
     fabric unit for measuring soil moisture, 217-232.  
     proportionate, of cations, 292.
- Alfalfa—  
     calcium-boron ratios for, 344.  
     influence of potassium and boron, 340.
- Amberlites, use in exchange studies, 377-384.
- Anion exchange, determination, 429-445.
- Basalt, soils developed from, in western Colorado, 365-375.
- Book reviews, *see* Books at end of letter B.
- Boron—  
     available in soils, 336.  
     content of alfalfa, as influenced by potassium, 340.  
     content of vegetative part of tomatoes, 67-71.  
     relation of calcium to, for alfalfa, 344.  
     requirements of West Virginia soils, 335-346.
- BOOKS
- Advances in Food Research, 467.
- Approach Toward a Rational Classification of Climate, 77.
- Baldwin, M., Buck, J. L., Greene, H., Lewis, A. B., Tsiang, T. C., Snow, S. B., Chambers, T. B., Steele, J. G., Kellogg, C. E., and Pendleton, R. L. Soil Conservation, an International Study, 81.
- Baver, L. D. Soil Physics, ed. 2, 162.
- Bennett, H. (Editor). Chemical Formulary, vol. 8, 239.
- Bibliography of the Literature on Sodium and Iodine, in Relation to Plant and Animal Nutrition, 467-468.
- Bibliography of the Literature on the Minor Elements and Their Relation to Plant and Animal Nutrition, vol. 1, ed. 4, 467.
- Blair, T. A. Weather Elements, ed. 3, 470.
- Bosazza, V. L. Petrography and Petrology of South African Clays, 162.
- Bromfield, L. Malabar Farm, 161.
- Buck, J. L. *See* Baldwin, M.
- Chambers, T. B. *See* Baldwin, M.
- Chemical Formulary, 239.
- Chemicals, Humus, and the Soil, 77.
- Clays, Petrography and Petrology of South African, 162.
- Climate, Approach Toward a Rational Classification of, 77.
- Cookability of Yellow Peas, 77.
- Corrie, F. E. Some Elements of Plants and Animals, 469-470.
- Crabb, A. R. Hybrid Corn Makers, 79.
- Crocker, W. Growth of Plants, 79.
- Crop production, Practical Field Crop Production for the Northeast, 80.
- Demolon, A. Dynamique du Sol, ed. 4, 77.
- Diehl, H. Electrochemical Analysis with Graded Cathode Potential Control, 78.
- Dynamique du Sol, 77.
- Electrochemical Analysis with Graded Cathode Potential Control, 78.
- Eruptive Rocks, 78.
- Farm Soils, Their Management and Fertilization, 468.
- Farming and Democracy, 239.
- Farnham, R. B., and Ingham, V. W. (Editors). Home Owner's Guide to Better Lawns, Trees, and Gardens, 161.
- Food Research, Advances in, 467.
- Forecasts of the Population of the United States 1945-1975, 78.
- Fundamentals of Soil Mechanics, 161.
- Gardens, Home Owner's Guide to Better Lawns, Trees, and, 161.
- Grass, the Yearbook of Agriculture, 1948, 468.
- Greene, H. *See* Baldwin, M.
- Griswold, A. W. Farming and Democracy, 239.
- Growth of Plants, 79.
- Haystead, L. Squires Can Take It, 162.
- Home Owner's Guide to Better Lawns, Trees, and Gardens, 161.
- Hopkins, D. P. Chemicals, Humus, and the Soil, 77.
- Hybrid Corn Makers, 79.
- Ingham, V. W. (Editor). Practical Field Crop Production for the Northeast, 80.
- Ingham, V. W. *See* Farnham, R. B.
- Isotopes, Preparation and Measurement of Isotopic Isomers, 80.
- Johnson, E. J. *See* Turner, A. W.
- Kellogg, C. E. *See* Baldwin, M.
- Land Economics, 468.
- Lawns, Trees, and Gardens, Home Owner's Guide to Better, 161.
- Lewis, A. B. *See* Baldwin, M.
- Machines for the Farm, Ranch and Plantation, 469.
- Malabar Farm, 161.
- Mattson, S. Cookability of Yellow Peas, 77.
- Mitchell, R. L. Spectrographic Analysis of Soils, Plants, and Related Materials, 240.
- Mrak, E. M., and Stewart, G. F. Advances in Food Research, vol. 1, 467.
- Odland, T. E. (chairman). Report of the Waste Conversion Committee of the State of Rhode Island and Providence Plantations, 81.
- Oosting, H. J. Study of Plant Communities, 163.
- Osborn, F. Our Plundered Planet, 239.
- Our Plundered Planet, 239.
- Pendleton, R. L. *See* Baldwin, M.
- Petrography and Petrology of South African Clays, 162.
- Plant and Soil, vol. 1, No. 1, 80.
- Plant Ecology, Study of Plant Communities, 163.
- Plants, Growth of, 79.
- Practical Field Crop Production for the Northeast, 80.
- Précis des Découvertes et Travaux Somiologiques, 469.
- Preparation and Measurement of Isotopic Isomers, 80.
- Proceedings of the Twenty-Third Annual Meeting of the National Joint Committee on Fertilizer Application, 469.
- Rafinesque-Schmaltz, C. S. Précis des Découvertes et Travaux Somiologiques 469.
- Renne, R. R. (Editor). Land Economics, 468.

- Report of the Waste Conversion Committee of the State of Rhode Island and Providence Plantations, 81
- Rocks, Eruptive, 78.
- Rothamsted Experimental Station Report for 1946, 240.
- Shand, S. J. *Eruptive Rocks*, ed. 3, 78.
- Snow, S. B. *See* Baldwin, M.
- Soil, Chemicals, Humus, and the, 77.
- Soil Conservation, an International Study, 81.
- Soil, *Dynamique du Sol*, 77.
- Soil Mechanics, Fundamentals of, 161.
- Soil Physics, 162.
- Soil, Plant and, 80.
- Some Elements of Plants and Animals, 469-470.
- Spectrographic Analysis of Soils, Plants, and Related Materials, 240.
- Squires Can Take It, 162.
- Steele, T. G. *See* Baldwin, M.
- Steffenrud, A. (Editor). *Grass, the Yearbook of Agriculture*, 1948, 468.
- Stewart, G. F. *See* Mrak, E. M.
- Study of Plant Communities, 163.
- Taxonomy, plant and animal, *Précis des Découvertes et Travaux Somnologiques*, 469.
- Taylor, D. W. *Fundamentals of Soil Mechanics*, 161.
- Thornthwaite, C. W. *Approach Toward a Rational Classification of Climate*, 77.
- Trees, Home Owner's Guide to Better Lawns, Trees, and Gardens, 161.
- Tsiang, T. C. *See* Baldwin, M.
- Turner, A. W., and Johnson, E. J. *Machines for the Farm, Ranch and Plantation*, 469.
- Weather Elements, 470.
- Whelpton, P. K. *Forecasts of the Population of the United States 1945-1975*, 78.
- Wilson, D. W. (Editor). *Preparation and Measurement of Isotopic Isomers*, 80.
- Works of French Agronomic Stations Between 1939 and 1945, 240.
- Worthen, E. L. *Farm Soils, Their Management and Fertilization*, 468.
- Calcium—**  
   boron ratios for alfalfa, 344.  
   content of vegetative part of tomatoes, 67-71.  
   ratio to boron in tomatoes, 72.
- Carbon—**  
   content of—  
     Colombia soils, 175.  
     soils after ten successive crops, 45.  
   effect of additions of green manures, 47.  
   nitrogen ratios, Colombia soils, 181.
- Cation exchange—**  
   comparison of methods for limed soils, 447-458.  
   determination, 429-445.  
   effect on cation content of plants, 289-306.
- Cation ratios—**  
   oats, 294.  
   soybeans, 293.  
   turnips, 294.
- Citrus soils—**  
   fertilization and steam sterilization, 276.  
   fumigation, 277.  
   inoculation, 284.  
   storage, effect on growth of seedlings, 283.  
   various cultural and fumigation treatments, effect on growth of orange seedlings in old, 273-288.
- Clay mineral models, construction and implications, 111-118.**
- Cleavage planes in lentil-structured black soils, 37**
- Colloids—**  
   dispersion in soil zones, 93.  
   relation to specific surface, 98.  
   vegetation as a peptizing factor, 91.
- Colombia—**  
   great soil groups of equatorial regions, 5-28.  
   nitrogen and organic matter contents of soils, 173-186.  
   soil groups in relation to climate, 10.
- Color of soils derived from basalt, 371.**
- Conrey, Guy Wollard, obituary, 171-172.**
- Copper—**  
   chemical and physical behavior in organic soils, 119-130.  
   effect of volatile disinfectants on exchangeable, 236.  
   extracted by nitric acid and ammonium acetate, 122.  
   fixation, 122.  
   replacement by hydrochloric acid, 124.  
   replacement of hydrogen by, 125.  
   sorption by organic soils, 123.  
   titration of copper-muck soils, 127.
- Critical stream, determination for various slopes, 205-216**
- Disinfectants, effect on—**  
   survival of microflora in soils, 233-238.  
   exchangeable copper and manganese, 236.
- Earthworms, influence on soil productivity, 421-428.**
- Embryonic soil, definition, 355.**
- Exchange complex properties of soil, 54-56.**
- Exchangeability of cations, as related to degree of saturation and nature, with reference to trace amounts, 377-384.**
- Fabric unit for measuring soil moisture—**  
   agronomic and hydrologic applications, 229.  
   performance characteristics, 225.
- Fertilizers, magnesium content, 147-154.**

- Fluorine, effects on, peach, tomato, and buckwheat when absorbed through roots, 259-266.
- Forest litter—  
weight and composition of Colombia, 183.  
weights in United States, 184.
- Green manures—  
effect of stage of maturity on carbon accumulation, 47.  
relation to nitrogen, 39-52.
- Gypsum—  
effect of—  
ions, 201.  
temperature, 202.  
rapid conductometric method for estimating, in soils, 199-204.
- Infiltration rates, as affected by earthworms, 426.
- Kaolinite structure, 111, 113, 114, 115.
- Ladino clover, absorption of potassium, 326.
- Lattice, expanding, montmorillonite, 115.
- Lime—  
effect on fixation of manganese, 133-134.  
requirement—  
relation to depression of pH, 58-60.  
testing with buffered solution and glass electrode, 53-63.
- Livingston, Burton Edward, obituary, 1-5.
- Magnesium—  
availability, 149.  
determination with thiazol yellow, 385-392.  
in fertilizers, soil amendments, and manures, 147-159.
- Manganese—  
behavior in soil, and its cycle, 131-146.  
cycle in soils, 142.  
effect of—  
bases and salts, 135.  
incubation temperature, 267-272.  
lime on fixation, 133-134.  
organic matter, 136-138, 268, 270.  
reducing agents, 138.  
sulfur on release, 135.  
volatile disinfectants on exchangeable, 236.
- Methods—  
boron, 335.  
gypsum, conductometric, 199-200.  
ion exchange, 429-445.  
lime requirement, 60.  
magnesium, plants and exchangeable, 385.  
mineral elements in plants, 459-466.  
moisture, fabric absorption, 219.
- Methods—(continued)  
moisture retention, porous plate, 105.  
molybdenum and rare earths in phosphate rocks, 317.  
organic matter, 241.
- Microorganisms—  
decomposition of water hyacinth, 401-420.  
effect of volatile disinfectants, 233-238.
- Millet, recovery of nitrogen by, 43.
- Moisture—  
curves, 220.  
cycles, 230.  
fabric unit for measuring soil, 217-232.  
porous plate method for measuring retention and transmission by soil, 105-110.
- Molybdenum—  
content of—  
dung, 193.  
plants, 188, 190, 191, 192, 198.  
soils, 189.  
determination in phosphate rock, 317-322.  
effect of, applications, 191-193.  
toxicity to animals, 187-196, 197-198.
- Montmorillonite structure, 111, 114, 115.
- Mulch—  
effect on moisture conservation and nitrate production, 307-315.  
straw, effect on recovery of nitrogen from sodium nitrate and ammonium sulfate top-dressing, 399-400.
- Muscovite structure, 115.
- Neubauer evaluation of organic phosphates, 253.
- Nitrogen—  
and soil color, 181-182.  
contents of—  
Colombia soils, 175.  
soils after ten successive crops, 45.  
elevation and temperature relationship, 177.  
rainfall relationships, 176.  
recovery in crops, 41.  
utilization in cropping systems with and without green manure, 39-52.
- Oats, absorption of potassium, 326.
- Organic matter—  
content of soils derived from basalt, 372.  
determination by colorimetric analysis, 241-247.  
effect on release of manganese, 136-138.  
magnesium content of, 154.
- Phosphates, organic, evaluation in pot cultures, 249-257.

- Plant growth regulators, persistence in soils—  
 influence of—  
   moisture, 395.  
   rates of application, 396.  
 isopropyl N-phenyl carbamate, 393-397.  
 Podzols, of Colombia, 12-14.  
 Potassium—  
   effects on boron in alfalfa, 340.  
   fixing power of soils, 330-331.  
   influence of lime on, uptake, 327.  
   radioactive, replacement, 381.  
   removal of exchangeable and nonexchangeable, 326.  
   supplying power of virgin and cropped soils, 323-334.  
 Psychrohumus soils, 11.  
 Pyranishnikov, Dimitrii Nikolaevich, obituary, 165-167.  
 Radioisotopes, use in exchange studies, 377-384.  
 Rainfall of Colombia, 6-7.  
 Rye, recovery of nitrogen by, 43.  
 Skeletal soil, definition, 354.  
 Soil series, analyses, descriptions of, or experiments with—  
   Aiken, 220; Altamont, 220; Antigo, 325, 335; Antioch, 220; Appling, 220; Berkeley, 336; Bermudian, 391; Bladen, 441, 447; Blago, 336; Billings, 201; Calhoun, 307; Calvin, 336; Carrington, 16, 325; Cayucos, 16, 189; Cecil, 220, 437, 440, 449; Chilhowie, 336; Clarion, 220, 440; Clarksville, 253; Clinton, 220, 226; Clymer, 336; Collington, 440, 449; Colma, 189; Cookport, 336; Craven, 447; Crosby, 220; Cumberland, 307, 399; Davidson, 441; Decatur, 220; Dunkirk, 220; Durham, 440; Esquatzel, 201; Evesboro, 40; Foster, 189; Frankstown, 336, 394; Frederick, 336; Gilpin, 336; Gleason, 189; Gloucester, 391; Grenada, 440; Hagerstown, 336; Halewood, 441; Hanford, 189; Hesperia, 189; Holland, 189, 220; Holtville, 201; Honeoye, 220; Houston, 440; Hyde, 447; Indio, 201; Iredell, 220; Lakewood, 391; Litz, 336; Los Osos, 189; Lufkin, 440; Marshall, 16; Maury, 220; Meigs, 336; Memphis, 220; Merced, 189; Merrimac, 234, 268; Miami, 220, 226, 325; Miles, 220; Mill  
   Soil series—(continued)  
   ville, 206, 211; Monongahela, 336; Moshannon, 337; Munjor, 220; Norfolk, 437; Oasis, 201, 213; Orangeburg, 440; Palouse, 220; Panoche, 189; Pickaway, 336; Plainfield, 220, 325; Portsmouth, 289, 437, 449; Putnam, 220, 449; Ramona, 274; Rardon, 336; Rayne, 336; Reagan, 201; Ruston, 299; Sagemoor, 201; San Joaquin, 220, 226; Sequatchie, 337; Shelby, 220; Sheridan, 189; Sierra, 189, 220; Spencer, 325; Superior, 325; Susquehanna, 440; Trenton, 213; Tumbez, 336; Tuxedo, 421; Umapine, 201; Upshur, 336; Vina, 220; Wabash, 220; Weller, 440; Wheeling, 337; Whippany, 391; White Store, 449; Wyatt, 337; Yolo, 189, 274, 281; Zoar, 336.  
   Soil tests, requirements for successful, 83-89.  
   Specific surface—  
     apparatus for measuring, 95.  
     relation between total colloid content and, 98.  
   Stony soils—  
     classification, 347-363.  
     definitions of—  
       grit, 349.  
       gravel, 351.  
       cobblestones, 351.  
       rubbles, 352.  
   Strontium, radioactive, replacement, 381.  
   Structure—  
     black cotton soils of India, 29-38.  
     effect of desiccation on, 33.  
     formation, 34.  
     kaolinite, 111.  
     lentil, 31.  
     measurement of soil, 97.  
     montmorillonite, 111.  
     muscovite, 115.  
     soils derived from basalt, 371.  
     variations of Yangambi soils, 91-104.  
   Sudan grass—  
     recovery of nitrogen by, 43.  
     response to organic phosphates, 254.  
   Sulfur, effect on release of manganese, 135.  
   Temperature, effect on exchangeable manganese, 267-272.  
   Titration curves of clays in presence of potassium chloride, 55.  
   Urea, recovery by crops, 44.

Vegetation, climatic distribution in Colombia, 7.

Water hyacinth—

breakdown in soils, 407.

decomposition with added ammonium nitrate, 405.

Water hyacinth—(*continued*)

microbiological decomposition, 401-420.

Wheat, recovery of nitrogen by, 43.

Yellow-brown humic soils of Colombia, 14-16.